LOW SPIN GOLF BALL
COMPRISING A METAL, CERAMIC, OR
COMPOSITE MANTLE OR INNER LAYER

Cross Reference to Related Applications

This application is a continuation application of U.S. application
Serial No. 09/248,860 filed February 11, 1999, which is a continuation-in-part
application of U.S. Application Serial No. 08/716,016 filed September 19, 1996,
which is a divisional of U.S. Application Serial No. 08/255,442 filed June 8,
1994, which is a continuation of U.S. Application Serial No. 08/054,406 filed
April 28, 1993. This application is also a continuation-in-part application of
U.S. Application Serial No. 09/027,482 filed February 20, 1998 which claims
priority from U.S. Provisional Application Serial No. 60/042,120 filed March 27,
1997; and U.S. Provisional Application 60/042,430 filed March 28, 1997; and
is a continuation-in-part application of U.S. Application Serial No. 08/714,661
filed September 16, 1996.

Field of the Invention

The present invention relates to golf balls and, more particularly,
to improved golf balls having low spin rates. The improvement in the golf balls
results from a combination of a relatively soft core, and a hard cover made from
blends of one or more specific hard, high stiffness ionomers. The combination
of a soft core and a hard cover leads to an improved golf ball having a lower
than anticipated spin rate while maintaining the resilience and durability
characteristics necessary for repetitive play.

In a particularly preferred embodiment, the present invention
relates to golf balls comprising one or more mantle layers formed from a metal,
ceramic, or a composite material. The golf balls may comprise an optional
polymeric outer cover and/or an inner polymeric hollow sphere substrate.

In an additional embodiment of the invention, the spin rate is
further reduced by decreasing the weight of the soft core while maintaining
core size and by increasing the thickness of the cover. The larger, less dense
finished ball exhibits lower spin rates after club impact than conventional balls.

Background of the Invention

Spin rate is an important golf ball characteristic for both the skilled and unskilled golfer. High spin rates allow for the more skilled golfer, such as PGA professionals and low handicap players, to maximize control of the golf ball. This is particularly beneficial to the more skilled golfer when hitting an approach shot to a green. The ability to intentionally produce "back spin", thereby stopping the ball quickly on the green, and/or "side spin" to draw or fade the ball, substantially improves the golfer's control over the ball. Thus, the more skilled golfer generally prefers a golf ball exhibiting high spin rate properties.

However, a high spin golf ball is not desirous by all golfers, particularly high handicap players who cannot intentionally control the spin of the ball. In this regard, less skilled golfers, have, among others, two substantial obstacles to improving their game: slicing and hooking. When a club head meets a ball, an unintentional side spin is often imparted which sends the ball off its intended course. The side spin reduces one's control over the ball as well as the distance the ball will travel. As a result, unwanted strokes are added to the game.

Consequently, while the more skilled golfer desires a high spin golf ball, a more efficient ball for the less skilled player is a golf ball that exhibits low spin properties. The low spin ball reduces slicing and hooking and enhances roll distance for the amateur golfer.

The present inventors have addressed the need for developing a golf ball having a reduced spin rate after club impact, while at the same time maintaining the durability, playability and resiliency characteristics needed for repetitive use. The reduced spin rate golf ball of the present invention meets the rules and regulations established by the United States Golf Association (U.S.G.A.).

Along these lines, the U.S.G.A. has set forth five (5) specific regulations to which a golf ball must conform. The U.S.G.A. rules require that a ball be no smaller than 1.680 inches in diameter. However, notwithstanding

this restriction, there is no specific limitation as to the maximum permissible diameter of a golf ball. As a result, a golf ball can be as large as desired so long as it is larger than 1.680 inches in diameter and so long as the other four (4) specific regulations are met.

The U.S.G.A. rules also require that balls weigh no more than 1.620 ounces, and that their initial velocity may not exceed 250 feet per second with a maximum tolerance of 2%, or up to 255 ft./sec. Further, the U.S.G.A. rules state that a ball may not travel a distance greater than 280 yards with a test tolerance of 6% when hit by the U.S.G.A. outdoor driving machine under specific conditions.

It has been determined by the present inventors that the combination of a relatively soft core (i.e. an overall core Riehle compression of about 75 to 160) and a hard cover (i.e. Shore D hardness of 65 or more) significantly reduces the overall spin rate of the resulting golf ball. The inventors have also learned that an increase in cover thickness, thereby increasing the overall diameter of the resulting golf ball, further reduces spin rate.

Top-grade golf balls sold in the United States may be generally classified as one of two types: two-piece or three-piece balls. The two-piece ball, exemplified by the balls sold by Spalding & Evenflo Companies, Inc. (the assignee of the present invention through its wholly owned subsidiary, Lisco, Inc.) under the trademark TOP-FLITE, consists of a solid polymeric core and a separately formed outer cover. The so-called three-piece balls, exemplified by the balls sold under the trademark TITLEIST by the Acushnet Company, consist of a liquid (e.g., TITLEIST TOUR 384) or solid (e.g., TITLEIST DT) center, elastomeric thread windings about the center, and a cover.

Spalding's two-piece golf balls are produced by molding a natural (balata) or synthetic (i.e. thermoplastic resin such as an ionomer resin) polymeric cover composition around a preformed polybutadiene (rubber) core. During the molding process, the desired dimple pattern is molded into the cover material. In order to reduce the number of coating steps involved in the finishing of the golf balls, a color pigment or dye and, in many instances, an optical brightener, are added directly to the generally "off white" colored

polymeric cover composition prior to molding By incorporating the pigment and/or optical brightener in the cover composition molded onto the golf ball core, this process eliminates the need for a supplemental pigmented painting step in order to produce a white or colored (notably orange, pink and yellow) golf ball.

With respect to multi-layered golf balls, Spalding is the leading manufacturer of two-piece golf balls in the world. Spalding manufactures over sixty (60) different types of two-piece balls which vary distinctly in such properties as playability (i.e. spin rate, compression, feel, etc.), travel distance (initial velocity, C.O.R., etc.), durability (impact, cut and weather resistance) and appearance (i.e. whiteness, reflectance, yellowness, etc.) depending upon the ball's core, cover and coating materials, as well as the ball's surface configuration (i.e. dimple pattern). Consequently, Spalding's two-piece golf balls offer both the amateur and professional golfer a variety of performance characteristics to suit an individual's game.

In regard to the specific components of a golf ball, although the nature of the cover can, in certain instances, make a significant contribution to the overall feel, spin (control), coefficient of restitution (C.O.R.) and initial velocity of a ball (see, for example, U.S. Patent 3,819,768 to Molitor), the initial velocity of two-piece and three-piece balls is determined mainly by the coefficient of restitution of the core. The coefficient of restitution of the core of wound (i.e. three-piece) balls can be controlled within limits by regulating the winding tension and the thread and center composition. With respect to two-piece balls, the coefficient of restitution of the core is a function of the properties of the elastomer composition from which it is made. The cover component of a golf ball is particularly influential in affecting the compression (feel), spin rates (control), distance (C.O.R.), and durability (i.e. impact resistance, etc.) of the resulting ball. Various cover compositions have been developed by Spalding and others in order to optimize the desired properties of the resulting golf balls.

Over the last twenty (20) years, improvements in cover and core material formulations and changes in dimple patterns have more or less continually improved golf ball distance. Top-grade golf balls, however, must meet several other important design criteria. To successfully compete in

today's golf ball market, a golf ball should be resistant to cutting and must be finished well; it should hold a line in putting and should have good click and feel. In addition, the ball should exhibit spin and control properties dictated by the skill and experience of the end user. Prior artisans have attempted to incorporate metal layers or metal filler particles in golf balls to alter the physical characteristics and performance of the balls. For example, U.S. Patent No. 3,031,194 to Strayer is directed to the use of a spherical inner metal layer that is bonded or otherwise adhered to a resilient inner constituent within the ball. The ball utilizes a liquid filled core. U.S. Patent No. 4,863,167 to Matsuki, et al. describes golf balls containing a gravity filler which may be formed from one or more metals disposed within a solid rubber-based core. U.S. Patent Nos. 4,886,275 and 4,995,613, both to Walker, disclose golf balls having a dense metal-containing core. U.S. Patent No. 4,943,055 to Corley is directed to a weighted warmup ball having a metal center.

Prior artisans have also described golf balls having one or more interior layers formed from a metal, and which feature a hollow center. Davis disclosed a golf ball comprising a spherical steel shell having a hollow air-filled center in U.S. Patent No. 697,816. Kempshall received numerous patents directed to golf balls having metal inner layers and hollow interiors, such as Patent Nos. 704,748; 704,838; 713,772; and 739,753. In U.S. Patent Nos. 1,182,604 and 1,182,605, Wadsworth described golf balls utilizing concentric spherical shells formed from tempered steel. U.S. Patent No. 1,568,514 to Lewis describes several embodiments for a golf ball, one of which utilizes multiple steel shells disposed within the ball, and which provide a hollow center for the ball.

As to the incorporation of glass or vitreous materials in golf balls, U.S. Patent No. 985,741 to Harvey discloses the use of a glass shell. Other artisans described incorporating glass microspheres within a golf ball such as in U.S. Patent No. 4,085,937 to Schenk.

In contrast, the use of polymeric materials in intermediate layers within a golf ball, is more popular than, for instance, the use of glass or other vitreous material. Kempshall disclosed the use of an interior coating layer of plastic in U.S. Patent Nos. 696,887 and 701,741. Kempshall further described

incorporating a fabric layer in conjunction with a plastic layer in U.S. Patent Nos. 696,891 and 700,656. Numerous subsequent approaches were patented in which a plastic inner layer was incorporated in a golf ball. A thermoplastic outer core layer was disclosed in U.S. Patent No. 3,534,965 to Harrison. Inner synthetic polymeric layers are noted in U.S. Patent No. 4,431,193 to Nesbitt. An inner layer of thermoplastic material surrounding a core is described in U.S. Patent No. 4,919,434 to Saito. An intermediate layer of an amide block polyether thermoplastic is disclosed in U.S. Patent No. 5,253,871 to Viellaz. Golf balls with thermoplastic interior shell layers are described in U.S. Patent No. 5,480,155 to Molitor, et al. Although satisfactory in many respects, these patents are not specifically directed to the use of reinforcement fibers or particles dispersed within a polymeric inner layer.

Prior artisans have attempted to incorporate various particles and filler materials into golf ball cores and intermediate layers. U.S. Patent No 3,218,075 to Shakespeare discloses a core of fiberglass particles dispersed within an epoxy matrix. Similarly, U.S. Patent No. 3,671,477 to Nesbitt discloses an epoxy-based composition containing a wide array of fillers. A rubber intermediate layer containing various metal fillers is noted in U.S. Patent 4,863,167 to Matsuki, et al. Similarly, a rubber inner layer having filler materials is noted in U.S. Patent No. 5,048,838 to Chikaraishi, et al. More recently, a golf ball with an inner layer of reinforced carbon graphite is disclosed in U.S. Patent No. 5,273,286 to Sun.

In view of the ever increasing demands of the current golf industry, there exists a need for yet another improved golf ball design and construction. Specifically, there is a need for a low spin golf ball that exhibits a high initial velocity or coefficient of restitution (COR), may be driven relatively long distances in regulation play, and which may be readily and inexpensively manufactured.

As previously noted, in an alternative embodiment, the spin rate of the ball is further reduced by increasing the thickness of the cover and/or decreasing the weight and softness of the core. By increasing the cover thickness and/or the overall diameter of the resulting molded golf ball, enhanced reduction in spin rate is observed.

With respect to the increased size of the ball, over the years golf ball manufacturers have generally produced golf balls at or around the minimum size and maximum weight specifications set forth by the U.S.G.A. There have, however, been exceptions, particularly in connection with the manufacture of golf balls for teaching aids. For example, oversized, overweight (and thus unauthorized) golf balls have been on sale for use as golf teaching aids (see U S. Patent 3,201,384 to Barber).

Oversized golf balls are also disclosed in New Zealand Patent No. 192,618 dated January 1, 1980, issued to a predecessor of the present assignee. This patent teaches an oversize golf ball having a diameter between 1.700 and 1.730 inches and an oversized core of resilient material (i.e. about 1.585 to 1.595 inches in diameter) so as to increase the coefficient of restitution. Additionally, the patent discloses that the ball should include a cover having a thickness less than the cover thickness of conventional balls (i.e. a cover thickness of about 0.050 inches as opposed to 0.090 inches for conventional two-piece balls).

In addition, it is also noted that golf balls made by Spalding in 1915 were of a diameter ranging from 1.630 inches to 1.710 inches. As the diameter of the ball increased, the weight of the ball also increased. These balls were comprised of covers made up of balata/gutta percha and cores made from solid rubber or liquid sacs and wound with elastic thread.

Golf balls known as the LYNX JUMBO were also commercially available by Lynx in October, 1979. These balls had a diameter of 1.76 to 1.80 inches. The LYNX JUMBO balls met with little or no commercial success. The balls consisted of a core comprised of wound core and a cover comprised of natural or synthetic balata.

However, notwithstanding the enhanced diameters of these prior golf balls, none of these balls produced the enhanced spin reduction characteristics and overall playability, distance and durability properties of the present invention and/or fall within the regulations set forth by the U.S.G.A. An object of the present invention is to produce a U.S.G.A. regulation golf ball having improved low spin properties while maintaining the resilience and durability characteristics necessary for repetitive play.

These and other objects and features of the invention will be apparent from the following summary and description of the invention and from the claims.

Summary of the Invention

The present invention is directed to improved golf balls having a low rate of spin upon club impact. The golf balls comprise a soft core and a hard cover. The hard cover may be sized to be larger than conventional diameters. The low spin rate enables the ball to travel a greater distance. In addition, the low spin rate provides the less skilled golfer with more control. This is because the low spin rate decreases undesirable side spin which leads to slicing and hooking. The combination of a hard cover and a soft core provides for a ball having a lower than anticipated spin rate while maintaining high resilience and good durability.

In a first aspect, the present invention provides a low spin golf ball comprising a core that includes a core component and a spherical mantle encompassing the core component. The mantle comprises a polymeric material and a reinforcing material dispersed throughout the polymeric material. The core exhibits a Riehle compression of at least about 75. The golf ball further comprises a polymeric outer cover disposed about the core. The cover may be formed from an array of different materials, but exhibits a Shore D hardness of at least about 65.

In another aspect, the present invention provides a golf ball comprising a core including a core component and a vitrous mantle enclosing the core component. The core has a Riehle compression of from about 75 to about 115. The low spin golf ball further comprises a polymeric outer cover disposed about the mantle. The cover has a Shore D hardness of at least about 65.

In another aspect, the present invention provides a low spin golf ball comprising a generally spherical core having an interior core component and a mantle layer disposed around the core component. The mantle layer is formed from a metal and the resulting core exhibits a Riehle compression of from about 75 to about 115. The golf ball further comprises a polymeric outer

cover disposed about the core   The cover exhibits a Shore D hardness of at least about 65.

Through the use of the softer cores and the hard cover, overall finished balls of the invention exhibit significantly lower spin rates than conventional balls of equal size and weight. Further, reduction in spin is also produced by increasing the thickness of the cover and by decreasing the weight of the softened core.

Further scope of the applicability of the present invention will become apparent from the detailed description given hereinafter. It should, however, be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art.

Brief Description of the Drawings

FIGURE 1 is a partial cross-sectional view of a first preferred embodiment low spin golf ball in accordance with the present invention, comprising a polymeric outer cover, one or more mantle layers, an optional polymeric hollow sphere substrate, and core material;

FIGURE 2 is a partial cross-sectional view of a second preferred embodiment low spin golf ball in accordance with the present invention, the golf ball comprising a polymeric outer cover, one or more mantle layers, and a core material;

FIGURE 3 is a partial cross-sectional view of a third preferred embodiment low spin golf ball in accordance with the present invention, the golf ball comprising one or more mantle layers and a core material;

FIGURE 4 is a partial cross-sectional view of a fourth preferred embodiment low spin golf ball in accordance with the present invention, the golf ball comprising one or more mantle layers, an optional polymeric hollow sphere substrate, and a core material;

FIGURE 5 is a partial cross-sectional view of a fifth preferred embodiment low spin golf ball in accordance with the present invention, the golf ball comprising a polymeric outer cover, a first mantle layer, a second mantle

layer, and a core material; and

FIGURE 6 is a partial cross-sectional view of a sixth preferred embodiment low spin golf ball in accordance with the present invention, the golf ball comprising a polymeric outer cover, a first and a second mantle layer in an alternate arrangement as compared to the embodiment illustrated in FIGURE 5, and a core material.

Detailed Description of the Preferred Embodiments

The present invention relates to the development of a golf ball having a low spin rate as a result of combining a relatively soft core and a hard cover. The present invention low spin golf balls feature a relatively soft interior core or core component. That is, the core and any interior mantle layers, collectively, exhibit a Riehle compression of at least about 75 and preferably from about 75 to about 160. Most preferably, the Riehle compression of the core is from about 80 to about 90. The present invention low spin golf balls also feature a relatively hard cover. That is, the cover exhibits a Shore D hardness of at least about 65. A lower spin rate after club impact contributes to straighter shots when the ball is mis-hit, greater efficiency in flight, and a lesser degree of energy loss on impact with the ground, adding increased roll or distance.

In addition, by increasing the diameter of the overall ball of the present invention beyond the U.S.G.A. minimum of 1.680 inches, the spin rate is still further decreased. In this embodiment of the invention, the ball, even though of larger diameter, uses substantially the same size core as a standard golf ball, the difference in size is provided by the additional thickness in the cover of the ball. This larger, low spin ball produces even greater control and flight efficiency than the standard size ball embodiment of the present invention.

In all the preferred embodiments noted herein, the golf balls preferably utilize a solid core or core component. It will be understood that the low spin golf balls may instead feature a hollow interior or hollow core. In addition, all preferred embodiment golf balls comprise one or more mantle layers that comprise one or more metals, ceramics, or composite materials. Details of the materials, configuration, and construction of each component in

the preferred embodiment golf balls are set forth below.

FIGURE 1 illustrates a first preferred embodiment low spin golf ball **100** in accordance with the present invention. It will be understood that the referenced drawings are not necessarily to scale. The first preferred embodiment golf ball **100** comprises an outermost polymeric outer cover **10**, one or more mantle layers **20**, an innermost polymeric hollow sphere substrate **30** and a core material **40**. the golf ball **100** provides a plurality of dimples **104** defined along an outer surface **102** of the golf ball **100**.

FIGURE 2 illustrates a second preferred embodiment low spin golf ball **200** in accordance with the present invention. The golf ball **200** comprises an outermost polymeric outer cover **10** and one or more mantle layers **20** and a core material **40**. The second preferred embodiment golf ball **200** provides a plurality of dimples **204** defined along the outer surface **202** of the ball.

FIGURE 3 illustrates a third preferred embodiment low spin golf ball **300** in accordance with the present invention. The golf ball **300** comprises one or more mantle layers **20** and a core material **40**. The golf ball **300** provides a plurality of dimples **304** defined along the outer surface **302** of the golf ball **300**.

FIGURE 4 illustrates a fourth preferred embodiment low spin golf ball **400** in accordance with the present invention. The golf ball **400** comprises one or more mantle layers **20**, an optional polymeric hollow sphere substrate **30**, and a core material **40**. The golf ball **400** provides a plurality of dimples **404** defined along the outer surface **402** of the golf ball **400**.

FIGURE 5 illustrates a fifth preferred embodiment low spin golf ball **500** in accordance with the present invention. The golf ball **500** comprises one or more mantle layers **20**, one or more mantle layers **50** of a material different than that in the mantle layers **20**, a cover **10**, and a core material **40**. The golf ball **500** has corresponding dimples as illustrated in FIGURES 1-4.

FIGURE 6 illustrates a sixth preferred embodiment low spin golf ball **600** in accordance with the present invention. The golf ball **600** is similar to the golf ball **500**, however, the mantle layers **20** and **50** are reversed.

In all the foregoing noted preferred embodiments, i.e. golf balls

100, 200, 300, 400, 500, and **600** the golf balls utilize a core or core component, such as core material **40**. It will be understood that all preferred embodiment golf balls may instead feature a hollow interior or hollow core. In addition, all preferred embodiment golf balls comprise one or more mantle layers, such as **20** and **50**, that comprise one or more metals, ceramics, or composite materials. And, it will be understood that all covers such as cover **10**, may be of a single or a multiple layer construction. Details of the materials, configuration, and construction of each component in the preferred embodiment golf balls are set forth below.

Riehle compression is a measurement of the deformation in thousandths of inches under a fixed static load of 200 pounds (a Riehle compression of 47 corresponds to a deflection under load of 0.047 inches).

PGA compression is determined by a force applied to a spring (i.e. 80 PGA = 80 Riehle; 90 PGA = 70 Riehle; and 100 PGA = 60 Riehle) manufactured by Atti Engineering, Union City, New Jersey.

Coefficient of restitution (C.O.R.) is measured by firing the resulting golf ball in an air cannon at a velocity of 125 feet per second against a steel plate which is positioned 12 feet from the muzzle of the cannon. The rebound velocity is then measured. The rebound velocity is divided by the forward velocity to give the coefficient of restitution.

Shore D hardness is measured in accordance with ASTM Test D-2240.

Core

In one aspect, the core used in the present invention golf ball is a specially produced softened polybutadiene elastomeric solid core having a conventional diameter of about 1.540 to 1.545 inches. The core is produced from a composition comprising a base elastomer selected from polybutadiene and mixtures of polybutadiene with other elastomers, at least one metallic salt of an unsaturated carboxylic acid (a co-crosslinking agent), and free radical initiator (a co-crosslinking agent). In addition, a suitable and compatible modifying ingredient including, but not limited to metal activators, fatty acids,

fillers, polypropylene powder and other additives may be included.

Of particular concern, only a limited amount of the metallic salt of an unsaturated carboxylic acid is included in the core compositions in order to produce the degree of core softness and weight desired. In this regard, it is

5   understood that when a larger overall ball is desired, the composition of the core is adjusted so that the molded finished ball falls within the weight parameters set forth by the U.S.G.A. Since the finished golf balls must still meet the U.S.G.A. weight limitation of 1.620 ounces, the core component of the larger and thicker covered balls are designed to be not only softer, but also

10 lighter in weight.

In such circumstances, the specific gravity of the core is less than that of a standard core since the larger ball must weigh the same as a standard ball. The core generally weighs about 36 to 37 grams for a standard sized finished ball and about 33 to 34 grams for an oversized finished ball.

15 The core composition produces a softer molded core which still maintains the resilience (C.O.R.), compression (hardness) and durability characteristics required. The overall core has a PGA compression of about 0 to 85, and preferably in the range of about 10 to about 70. Its Riehle compression is about 75 or more, preferably in the range of about 75 to about

20 160, and the resilience of the core is about 0.760 to 0.780.

The specially produced core compositions and resulting molded cores of the present invention are manufactured using relatively conventional techniques. In this regard, the core compositions of the invention may be based on polybutadiene, and mixtures of polybutadiene with other elastomers.

25 It is preferred that the base elastomer have a relatively high molecular weight. The broad range for the molecular weight of suitable base elastomers is from about 50,000 to about 500,000. A more preferred range for the molecular weight of the base elastomer is from about 100,000 to about 500,000. As a base elastomer for the core composition, cis-polybutadiene is preferably

30 employed, or a blend of cis-polybutadiene with other elastomers may also be utilized. Most preferably, cis-polybutadiene having a weight-average molecular weight of from about 100,000 to about 500,000 is employed. Along this line, it has been found that the high cis-polybutadiene manufactured and sold by Shell

Chemical Co , Houston, Texas, under the tradename Cariflex BR-1220, and the polyisoprene available from Muehlstein, H & Co., Greenwich, Connecticut under the designation "SKI 35" are particularly well suited.

The unsaturated carboxylic acid component of the core composition (a co-crosslinking agent) is the reaction product of the selected carboxylic acid or acids and an oxide or carbonate of a metal such as zinc, magnesium, barium, calcium, lithium, sodium, potassium, cadmium, lead, tin, and the like. Preferably, the oxides of polyvalent metals such as zinc, magnesium and cadmium are used, and most preferably, the oxide is zinc oxide.

Exemplary of the unsaturated carboxylic acids which find utility in the present core compositions are acrylic acid, methacrylic acid, itaconic acid, crotonic acid, sorbic acid, and the like, and mixtures thereof. Preferably, the acid component is either acrylic or methacrylic acid. Usually, from about 15 to about 25, and preferably from about 17 to about 21 parts by weight of the carboxylic acid salt, such as zinc diacrylate, is included in the core composition. The unsaturated carboxylic acids and metal salts thereof are generally soluble in the elastomeric base, or are readily dispersible.

The free radical initiator included in the core composition is any known polymerization initiator (a co-crosslinking agent) which decomposes during the cure cycle. The term "free radical initiator" as used herein refers to a chemical which, when added to a mixture of the elastomeric blend and a metal salt of an unsaturated, carboxylic acid, promotes crosslinking of the elastomers by the metal salt of the unsaturated carboxylic acid. The amount of the selected initiator present is dictated only by the requirements of catalytic activity as a polymerization initiator. Suitable initiators include peroxides, persulfates, azo compounds and hydrazides. Peroxides which are readily commercially available are conveniently used in the present invention, generally in amounts of from about 0.1 to about 10.0 and preferably in amounts of from about 0.3 to about 3.0 parts by weight per each 100 parts of elastomer.

Exemplary of suitable peroxides for the purposes of the present invention are dicumyl peroxide, n-butyl 4,4'-bis (butylperoxy) valerate, 1,1-bis(t-butylperoxy)-3,3,5-trimethyl cyclohexane, di-t-butyl peroxide and 2,5-di-(t-

butylperoxy)-2,5 dimethyl hexane and the like, as well as mixtures thereof. It will be understood that the total amount of initiators used will vary depending on the specific end product desired and the particular initiators employed.

Examples of such commercially available peroxides are Luperco 230 or 231 XL sold by Atochem, Lucidol Division, Buffalo, N.Y., and Trigonox 17/40 or 29/40 sold by Akzo Chemie America, Chicago, Illinois. In this regard Luperco 230 XL and Trigonox 17/40 are comprised of n-butyl 4,4-bis (butylperoxy) valerate; and, Luperco 231 XL and Trigonox 29/40 are comprised of 1,1-bis(t-butylperoxy)-3,3,5-trimethyl cyclohexane. The one hour half life of Luperco 231 XL and Trigonox 29/40 is about 112°C, and the one hour half life of Luperco 230 XL and Trigonox 17/40 is about 129 °C.

The core compositions of the present invention may additionally contain any other suitable and compatible modifying ingredients including, but not limited to, metal oxides, fatty acids, and diisocyanates and polypropylene powder resin. For example, Papi 94, a polymeric diisocyanate, commonly available from Dow Chemical Co., Midland, Michigan., is an optional component in the rubber compositions. It can range from about 0 to 5 parts by weight per 100 parts by weight rubber (phr) component, and acts as a moisture scavenger. In addition, it has been found that the addition of a polypropylene powder resin results in a core which is too hard (i.e. exhibits low compression) and thus allows for a reduction in the amount of crosslinking agent utilized to soften the core to a normal or below normal compression.

Furthermore, because polypropylene powder resin can be added to the core composition without an increase in weight of the molded core upon curing, the addition of the polypropylene powder allows for the addition of higher specific gravity fillers, such as mineral fillers. Since the crosslinking agents utilized in the polybutadiene core compositions are expensive and/or the higher specific gravity fillers are relatively inexpensive, the addition of the polypropylene powder resin substantially lowers the cost of the golf ball cores while maintaining, or lowering, weight and compression.

The polypropylene (C_3H_5) powder suitable for use in the present invention has a specific gravity of about 0.90 g/cm^3, a melt flow rate of about 4 to about 12 and a particle size distribution of greater than 99% through a 20

mesh screen. Examples of such polypropylene powder resins include those sold by the Amoco Chemical Co., Chicago, Illinois, under the designations "6400 P", "7000 P" and "7200 P". Generally, from 0 to about 25 parts by weight polypropylene powder per each 100 parts of elastomer are included in the present invention.

Various activators may also be included in the compositions of the present invention. For example, zinc oxide and/or magnesium oxide are activators for the polybutadiene. The activator can range from about 2 to about 30 parts by weight per 100 parts by weight of the rubber (phr) component.

Moreover, filler-reinforcement agents may be added to the core composition of the present invention. Since the specific gravity of polypropylene powder is very low, and when compounded, the polypropylene powder produces a lighter molded core, when polypropylene is incorporated in the core compositions, relatively large amounts of higher gravity fillers may be added so long as the specific core weight limitations are met. Additional benefits may be obtained by the incorporation of relatively large amounts of higher specific gravity, inexpensive mineral fillers such as calcium carbonate. Such fillers as are incorporated into the core compositions should be in finely divided form, as for example, in a size generally less than about 30 mesh and preferably less than about 100 mesh U.S. standard size. The amount of additional filler included in the core composition is primarily dictated by weight restrictions and preferably is included in amounts of from about 10 to about 100 parts by weight per 100 parts rubber.

The preferred fillers are relatively inexpensive and heavy and serve to lower the cost of the ball and to increase the weight of the ball to closely approach the U.S.G.A. weight limit of 1.620 ounces. However, if thicker cover compositions are to be applied to the core to produce larger than normal (i.e. greater than 1.680 inches in diameter) balls, use of such fillers and modifying agents will be limited in order to meet the U.S.G.A. maximum weight limitations of 1.620 ounces. Exemplary fillers include mineral fillers such as limestone, silica, micabarytes, calcium carbonate, or clays. Limestone is ground calcium/magnesium carbonate and is used because it is an inexpensive, heavy filler.

As indicated, ground flash filler may be incorporated and is preferably 20 mesh ground up center stock from the excess flash from compression molding. The use of such filler lowers the cost and may increase the hardness of the ball.

Fatty acids or metallic salts of fatty acids may also be included in the core compositions, functioning to improve moldability and processing. Generally, free fatty acids having from about 10 to about 40 carbon atoms, and preferably having from about 15 to about 20 carbon atoms, are used. Exemplary of suitable fatty acids are stearic acid and linoleic acids, as well as mixtures thereof. Exemplary of suitable metallic salts of fatty acids include zinc stearate. When included in the core compositions, the fatty acid component is present in amounts of from about 1 to about 25, preferably in amounts from about 2 to about 15 parts by weight based on 100 parts rubber (elastomer).

It is preferred that the core compositions include stearic acid as the fatty acid adjunct in an amount of from about 2 to about 5 parts by weight per 100 parts of rubber.

Diisocyanates may also be optionally included in the core compositions when utilized, the diioscyanates are included in amounts of from about 0.2 to about 5.0 parts by weight based on 100 parts rubber. Exemplary of suitable diisocyanates is 4,4'-diphenylmethane diisocyanate and other polyfunctional isocyanates know to the art.

Furthermore, the dialkyl tin difatty acids set forth in U.S. Patent No. 4,844,471, the dispersing agents disclosed in U.S. Patent No. 4,838,556, and the dithiocarbamates set forth in U.S. Patent No. 4,852,884 may also be incorporated into the polybutadiene compositions of the present invention. The specific types and amounts of such additives are set forth in the above identified patents, which are incorporated herein by reference.

The core compositions of the invention are generally comprised of 100 parts by weight of a base elastomer (or rubber) selected from polybutadiene and mixtures of polybutadiene with other elastomers, 15 to 25 parts by weight of at least one metallic salt of an unsaturated carboxylic acid, and 1 to 10 parts by weight of a free radical initiator.

As indicated above, additional suitable and compatible modifying

agents such as particulate polypropylene resin, fatty acids, and secondary additives such as Pecan shell flour, ground flash (i.e. grindings from previously manufactured cores of substantially identical construction), barium sulfate, zinc oxide, etc. may be added to the core compositions to adjust the weight of the ball as necessary in order to have the finished molded ball (core, cover and coatings) to closely approach the U.S.G.A. weight limit of 1.620 ounces.

In producing golf ball cores utilizing the present compositions, the ingredients may be intimately mixed using, for example, two roll mills or a Banbury mixer until the composition is uniform, usually over a period of from about 5 to about 20 minutes. The sequence of addition of components is not critical. A preferred blending sequence is as follows.

The elastomer, polypropylene powder resin (if desired), fillers, zinc salt, metal oxide, fatty acid, and the metallic dithiocarbamate (if desired), surfactant (if desired), and tin difatty acid (if desired), are blended for about 7 minutes in an internal mixer such as a Banbury mixer. As a result of shear during mixing, the temperature rises to about 200°F. The initiator and diisocyanate are then added and the mixing continued until the temperature reaches about 220°F whereupon the batch is discharged onto a two roll mill, mixed for about one minute and sheeted out.

The sheet is rolled into a "pig" and then placed in a Barwell preformer and slugs are produced. The slugs are then subjected to compression molding at about 320°F for about 14 minutes. After molding, the molded cores are cooled, the cooling effected at room temperature for about 4 hours or in cold water for about one hour. The molded cores are subjected to a centerless grinding operation whereby a thin layer of the molded core is removed to produce a round core having a diameter of 1.540 to 1.545 inches. Alternatively, the cores are used in the as-molded state with no grinding needed to achieve roundness.

The mixing is desirably conducted in such a manner that the composition does not reach incipient polymerization temperatures during the blending of the various components.

Usually the curable component of the composition will be cured by heating the composition at elevated temperatures on the order of from about

275°F to about 350°F, preferably and usually from about 290°F to about 325°F, with molding of the composition effected simultaneously with the curing thereof. The composition can be formed into a core structure by any one of a variety of molding techniques, e.g. injection, compression, or transfer molding. When the composition is cured by heating, the time required for heating will normally be short, generally from about 10 to about 20 minutes, depending upon the particular curing agent used. Those of ordinary skill in the art relating to free radical curing agents for polymers are conversant with adjustments of cure times and temperatures required to effect optimum results with any specific free radical agent.

After molding, the core is removed from the mold and the surface thereof, preferably treated to facilitate adhesion thereof to the covering materials. Surface treatment can be effected by any of the several techniques known in the art, such as corona discharge, ozone treatment, sand blasting, and the like. Preferably, surface treatment is effected by grinding with an abrasive wheel.

The core is converted into a golf ball by providing at least one layer of covering material thereon, ranging in thickness from about 0.070 to about 0.130 inches and preferably from about 0.0675 to about 0.1275 inches.

In another aspect, the present invention golf ball may utilize a wound core as known in the art. Descriptions of wound cores and their manufacture are found in the following U.S. patents: 5,792,008; 5,755,628; 5,685,785; 5,630,562; 5,609,532; 5,007,594; 4,846,910; and 4,272,079; all of which are herein incorporated by reference.

Mantle

The preferred embodiment low spin golf balls of the present invention comprise one or more mantle layers disposed inwardly and proximate to, and preferably adjacent to, the outer cover layer which is described in greater detail herein. The mantle layer(s) may be formed from metal, ceramic, or composite materials. Regarding metals, a wide array of metals can be used in the mantle layers or shells as described herein. Table 1, set forth below, lists suitable metals for use in the preferred embodiment golf balls.

TABLE 1

Metals for Use in Mantle Layer(s)

Metal	Young's modulus, E, 10^6 psi	Bulk modulus, K, 10^6 psi	Shear modulus, G, 10^6 psi	Poisson's ratio, v
Aluminum	10 2	10 9	3 80	0 345
Brass, 30 Zn	14 6	16.2	5 41	0.350
Chromium	40 5	23 2	16 7	0.210
Copper	18 8	20 0	7 01	0.343
Iron (soft)	30 7	24 6	11 8	0.293
(cast)	22 1	15.9	8.7	0.27
Lead	2 34	6 64	0.811	0.44
Magnesium	6 48	5 16	2 51	0.291
Molybdenum	47 1	37 9	18 2	·0 293
Nickel (soft)	28 9	25 7	11.0	0 312
(hard)	31 8	27 2	12.2	0 306
Nickel-silver, 55Cu-18Ni-27Zn	19 2	19 1	4 97	0 333
Niobium	15 2	24 7	5 44	0 397
Silver	12 0	15 0	4 39	0 367
Steel, mild	30 7	24 5	11 9	0 291
Steel, 0.75 C	30 5	24 5	11.8	0.293
Steel, 0 75 C, hardened	29 2	23 9	11.3	0 296
Steel, tool	30 7	24 0	11.9	0.287
Steel, tool, hardened	29 5	24 0	11.4	0.295
Steel, stainless, 2Ni-18Cr	31 2	24 1	12 2	0.283
Tantalum	26 9	28.5	10.0	0.342
Tin	7 24	8.44	2.67	0.357
Titanium	17 4	15.7	6.61	0.361
Titanium/Nickel alloy				
Tungsten	59 6	45 1	23 3	0.280
Vanadium	18 5	22.9	6.77	0.365
Zinc	15 2	10 1	6 08	0.249

Preferably, the metals used in the one or more mantle layers are steel, titanium, chromium, nickel, or alloys thereof. Generally, it is preferred that the metal selected for use in the mantle be relatively stiff, hard, dense, and have a relatively high modulus of elasticity.

The thickness of the metal mantle layer depends upon several factors, such as the density of the metals used in that layer, or if a plurality of metal mantle layers are used, the densities of those metals in other layers within the mantle. Typically, the thickness of the mantle ranges from about

5 0.001 inches to about 0.050 inches. The preferred thickness for the mantle is from about 0.005 inches to about 0.050 inches. The most preferred range is from about 0.005 inches to about 0.010 inches. It is preferred that the thickness of the mantle be uniform and constant at all points across the mantle.

As noted, the thickness of the metal mantle depends upon the

10 density of the metal(s) utilized in the one or more mantle layers. Table 2, set forth below, lists typical densities for the preferred metals for use in the mantle.

TABLE 2

Metal	Density (grams per cubic centimeter)
Chromium	6.46
Nickel	7.90
Steel (approximate)	7.70
Titanium	4.13

There are at least two approaches in forming a metal mantle utilized in the preferred embodiment golf balls. In a first embodiment, two metal

20 half shells are stamped from metal sheet stock. The two half shells are then arc welded together and heat treated to stress relieve. It is preferred to heat treat the resulting assembly since welding will typically anneal and soften the resulting hollow sphere resulting in "oil canning," i.e. deformation of the metal sphere after impact, such as may occur during play.

25 In a second embodiment, a metal mantle is formed via electroplating over a thin hollow polymeric sphere, described in greater detail below. This polymeric sphere may correspond to an optional polymeric hollow sphere substrate described in greater detail herein . There are several preferred techniques by which a metallic mantle layer may be deposited upon

30 a non-metallic substrate. In a first category of techniques, an electrically conductive layer is formed or deposited upon the polymeric or non-metallic sphere. Electroplating may be used to fully deposit a metal layer after a

conductive salt solution is applied onto the surface of the non-metallic substrate. Alternatively, or in addition, a thin electrically conducting metallic surface can be formed by flash vacuum metallization of a metal agent, such as aluminum, onto the substrate of interest. Such surfaces are typically about 3

5   x 10^{-6} of an inch thick. Once deposited, electroplating can be utilized to form the metal layer(s) of interest. It is contemplated that vacuum metallization could be employed to fully deposit the desired metal layer(s). Yet another technique for forming an electrically conductive metal base layer is chemical deposition. Copper, nickel, or silver, for example, may be readily deposited upon a non-

10   metallic surface. Yet another technique for imparting electrical conductivity to the surface of a non-metallic substrate is to incorporate an effective amount of electrically conductive particles in the substrate, such as carbon black, prior to molding. Once having formed an electrically conductive surface, electroplating processes can be used to form the desired metal mantle layers.

15   Alternatively, or in addition, various thermal spray coating techniques can be utilized to form one or more metal mantle layers onto a spherical substrate. Thermal spray is a generic term generally used to refer to processes for depositing metallic and non-metallic coatings, sometimes known as metallizing, that comprise the plasma arc spray, electric arc spray, and flame

20   spray processes. Coatings can be sprayed from rod or wire stock, or from powdered material.

A typical plasma arc spray system utilizes a plasma arc spray gun at which one or more gasses are energized to a highly energized state, i.e. a plasma, and are then discharged typically under high pressures toward the

25   substrate of interest. The power level, pressure, and flow of the arc gasses, and the rate of flow of powder and carrier gas are typically control variables.

The electric arc spray process preferably utilizes metal in wire form. This process differs from the other thermal spray processes in that there is no external heat source, such as from a gas flame or electrically induced

30   plasma. Heating and melting occur when two electrically opposed charged wires, comprising the spray material, are fed together in such a manner that a controlled arc occurs at the intersection. The molten metal is atomized and propelled onto a prepared substrate by a stream of compressed air or gas.

The flame spray process utilizes combustible gas as a heat source to melt the coating material. Flame spray guns are available to spray materials in rod, wire, or powder form. Most flame spray guns can be adapted for use with several combinations of gases. Acetylene, propane, mapp gas,

5   and oxygen-hydrogen are commonly used flame spray gases.

Another process or technique for depositing a metal mantle layer onto a spherical substrate in the preferred embodiment golf balls is chemical vapor deposition (CVD). In the CVD process, a reactant atmosphere is fed into a processing chamber where it decomposes at the surface of the substrate of

10 interest, liberating one material for either absorption by or accumulation on the work piece or substrate. A second material is liberated in gas form and is removed from the processing chamber, along with excess atmosphere gas, as a mixture referred to as off-gas.

The reactant atmosphere that is typically used in CVD includes

15 chlorides, fluorides, bromides and iodides, as well as carbonyls, organometallics, hydrides and hydrocarbons. Hydrogen is often included as a reducing agent. The reactant atmosphere must be reasonably stable until it reaches the substrate, where reaction occurs with reasonably efficient conversion of the reactant. Sometimes it is necessary to heat the reactant to

20 produce the gaseous atmosphere. A few reactions for deposition occur at substrate temperatures below 200 degrees C. Some organometallic compounds deposit at temperatures of 600 degrees C. Most reactions and reaction products require temperatures above 800 degrees C.

Common CVD coatings include nickel, tungsten, chromium, and

25 titanium carbide. CVD nickel is generally separated from a nickel carbonyl, $Ni(CO)_4$, atmosphere. The properties of the deposited nickel are equivalent to those of sulfonate nickel deposited electrolytically. Tungsten is deposited by thermal decomposition of tungsten carbonyl at 300 to 600 degrees C, or may be deposited by hydrogen reduction of tungsten hexachloride at 700 to 900

30 degrees C. The most convenient and most widely used reaction is the hydrogen reduction of tungsten hexafluoride. If depositing chromium upon an existing metal layer, this may be done by pack cementation, a process similar to pack carbonizing, or by a dynamic, flow-through CVD process. Titanium

carbide coatings may be formed by the hydrogen reduction of titanium tetrafluoride in the presence of methane or some other hydrocarbon. The substrate temperatures typically range from 900 to 1010 degrees C, depending on the substrate.

Surface preparation for CVD coatings generally involve degreasing or grit blasting. In addition, a CVD pre-coating treatment may be given. The rate of deposition from CVD reactions generally increases with temperature in a manner specific to each reaction. Deposition at the highest possible rate is preferable, however, there are limitations which require a processing compromise.

Vacuum coating is another category of processes for depositing metals and metal compounds from a source in a high vacuum environment onto a substrate, such as the spherical substrate used in several of the preferred embodiment golf balls. Three principal techniques are used to accomplish such deposition: evaporation, ion plating, and sputtering. In each technique, the transport of vapor is carried out in an evacuated, controlled environment chamber and, typically, at a residual air pressure of 1 to 10^{-5} Pascals.

In the evaporation process, vapor is generated by heating a source material to a temperature such that the vapor pressure significantly exceeds the ambient chamber pressure and produces sufficient vapor for practical deposition. To coat the entire surface of a substrate, such as the inner spherical substrate utilized in the preferred embodiment golf balls, it must be rotated and translated over the vapor source. Deposits made on substrates positioned at low angles to the vapor source generally result in fibrous, poorly bonded structures. Deposits resulting from excessive gas scattering are poorly adherent, amorphous, and generally dark in color. The highest quality deposits are made on surfaces nearly normal or perpendicular to the vapor flux. Such deposits faithfully reproduce the substrate surface texture. Highly polished substrates produce lustrous deposits, and the bulk properties of the deposits are maximized for the given deposition conditions.

For most deposition rates, source material should be heated to a temperature so that its vapor pressure is at least 1 Pascal or higher. Deposition rates for evaporating bulk vacuum coatings can be very high. Commercial

coating equipment can deposit up to 500,000 angstroms of material thickness per minute using large ingot material sources and high powered electron beam heating techniques.

As indicated, the directionality of evaporating atoms from a vapor source generally requires the substrate to be articulated within the vapor cloud. To obtain a specific film distribution on a substrate, the shape of the object, the arrangement of the vapor source relative to the component surfaces, and the nature of the evaporation source may be controlled.

Concerning evaporation sources, most elemental metals, semi-conductors, compounds, and many alloys can be directly evaporated in vacuum. The simplest sources are resistance wires and metal foils. They are generally constructed of refractory metals, such as tungsten, molybdenum, and tantalum The filaments serve the dual function of heating and holding the material for evaporation Some elements serve as sublimation sources such as chromium, palladium, molybdenum, vanadium, iron, and silicon, since they can be evaporated directly from the solid phase. Crucible sources comprise the greatest applications in high volume production for evaporating refractory metals and compounds. The crucible materials are usually refractory metals, oxides, and nitrides, and carbon. Heating can be accomplished by radiation from a second refractory heating element, by a combination of radiation and conduction, and by radial frequency induction heating.

Several techniques are known for achieving evaporation of the evaporation source. Electron beam heating provides a flexible heating method that can concentrate heat on the evaporant. Portions of the evaporant next to the container can be kept at low temperatures, thus minimizing interaction. Two principal electron guns in use are the linear focusing gun, which uses magnetic and electrostatic focusing methods, and the bent-beam magnetically focused gun. Another technique for achieving evaporation is continuous feed high rate evaporation methods High rate evaporation of alloys to form film thicknesses of 100 to 150 micrometers requires electron beam heating sources in large quantities of evaporant. Electron beams of 45 kilowatts or higher are used to melt evaporants in water cooled copper hearths up to 150 by 400 millimeters in cross section.

Concerning the substrate material of the spherical shell upon which one or more metal layers are formed in the preferred embodiment golf balls, the primary requirement of the material to be coated is that it be stable in vacuum. It must not evolve gas or vapor when exposed to the metal vapor. Gas evolution may result from release of gas absorbed on the surface, release of gas trapped in the pores of a porous substrate, evolution of a material such as plasticizers used in plastics, or actual vaporization of an ingredient in the substrate material.

In addition to the foregoing methods, sputtering may be used to deposit one or more metal layers onto, for instance, an inner hollow sphere substrate such as substrate 30 utilized in the preferred embodiment golf balls. Sputtering is a process wherein material is ejected from the surface of a solid or liquid because of a momentum exchange associated with bombardment by energetic particles. The bombarding species are generally ions of a heavy inert gas. Argon is most commonly used. The source of ions may be an ion beam or a plasma discharge into which the material can be bombarded is immersed.

In the plasma-discharge sputter coating process, a source of coating material called a target is placed in a vacuum chamber which is evacuated and then back filled with a working gas, such as Argon, to a pressure adequate to sustain the plasma discharge. A negative bias is then applied to the target so that it is bombarded by positive ions from the plasma.

Sputter coating chambers are typically evacuated to pressures ranging from 0.001 to 0.00001 Pascals before back filling with Argon to pressures of 0.1 to 10 Pascals. The intensity of the plasma discharge, and thus the ion flux and sputtering rate that can be achieved, depends on the shape of the cathode electrode, and on the effective use of a magnetic field to confine the plasma electrons. The deposition rate in sputtering depends on the target sputtering rate and the apparatus geometry. It also depends on the working gas pressure, since high pressures limit the passage of sputtered flux to the substrates.

Ion plating may also be used to form one or more metal mantle layers in the golf balls of the present invention. Ion plating is a generic term applied to atomistic film deposition processes in which the substrate surface

and/or the depositing film is subjected to a flux of high energy particles (usually gas ions) sufficient to cause changes in the interfacial region or film properties. Such changes may be in the film adhesion to the substrate, film morphology, film density, film stress, or surface coverage by the depositing film material.

Ion plating is typically done in an inert gas discharge system similar to that used in sputtering deposition except that the substrate is the sputtering cathode and the bombarded surface often has a complex geometry. Basically, the ion plating apparatus is comprised of a vacuum chamber and a pumping system, which is typical of any conventional vacuum deposition unit. There is also a film atom vapor source and an inert gas inlet. For a conductive sample, the work piece is the high voltage electrode, which is insulated from the surrounding system. In the more generalized situation, a work piece holder is the high voltage electrode and either conductive or non-conductive materials for plating are attached to it. Once the specimen to be plated is attached to the high voltage electrode or holder and the filament vaporization source is loaded with the coating material, the system is closed and the chamber is pumped down to a pressure in the range of .001 to .0001 Pascals. When a desirable vacuum has been achieved, the chamber is back filled with Argon to a pressure of approximately 1 to 0.1 Pascals. An electrical potential of -3 to -5 kilovolts is then introduced across the high voltage electrode, that is the specimen or specimen holder, and the ground for the system. Glow discharge occurs between the electrodes which results in the specimen being bombarded by the high energy Argon ions produced in the discharge, which is equivalent to direct current sputtering. The coating source is then energized and the coating material is vaporized into the glow discharge.

Another class of materials, contemplated for use in forming the one or more metal mantle layers is nickel titanium alloys. These alloys are known to have super elastic properties and are approximately 50 percent (atomic) nickel and 50 percent titanium. When stressed, a super elastic nickel titanium alloy can accommodate strain deformations of up to 8 percent. When the stress is later released, the super elastic component returns to its original shape. Other shape memory alloys can also be utilized including alloys of copper zinc aluminum, and copper aluminum nickel. Table 3 set forth below

presents various physical, mechanical, and transformation properties of these three preferred shape memory alloys

TABLE 3

Properties of Shape Memory Alloys
for Use in Mantle Layer(s)

PHYSICAL PROPERTIES	Cu-Zn-Al	Cu-Al-Ni	Ni-Ti
Density (g/cm³)	7 64	7 12	6 5
Resistivity (µΩ-cm)	8 5-9 7	11-13	80-100
Thermal Conductivity (J/m-s-K)	120	30-43	10
Heat Capacity (J/Kg-K)	400	373-574	390
			.
MECHANICAL PROPERTIES	Cu-Zn-al	Cu-Al-Ni	Ni-Ti
Young's Modulus (GPa)			
β-Phase	72	85	83
Martensite	70	80	34
Yield Strength (MPa)			
β-Phase	350	400	690
Martensite	80	130	70-150
Ultimate Tensile Strength (Mpa)	600	500-800	900
TRANSFORMATION PROPERTIES	Cu-Zn-Al	Cu-Al-Ni	Ni-Ti
Heat of Transformation (J/mole)			
Martensite	160-440	310-470	
R-Phase			55
Hysteresis (K)			
Martensite	10-25	15-20	30-40
R-Phase			2-5
Recoverable Strain (%)			
One-Way (Martensite)	4	4	8
One-Way (R-Phase			0 5-1
Two-Way (Martensite)	2	2	3

As noted, the previously-described mantle may also comprise one or more ceramic or vitreous materials. Preferred ceramics include, but are not limited to, silica, soda lime, lead silicate, borosilicate, aluminoborosilicate, aluminosilicate, and various glass ceramics. Specifically, a wide array of

ceramic materials can be utilized in the ceramic mantle layer. Table 4 set forth below provides a listing of suitable ceramic materials.

TABLE 4

Ceramics for Use in Mantle Layer(s)

Material	Modulus of rupture, MPa
aluminum oxide crystals	345-1034
sintered alumina (ca 5% porosity)	207-345
alumina porcelain (90-95% Al_2O_3)	345
sintered beryllia (ca 5% porosity)	138-276
hot-pressed boron nitride (ca 5% porosity)	48-103
hot-pressed boron carbide (ca 5% porosity)	345
sintered magnesia (ca 5% porosity)	103
sintered molybdenum silicide (ca 5% porosity)	690
sintered spinel (ca 5% porosity)	90
dense silicon carbide (ca 5% porosity)	172
sintered titanium carbide (ca 5% porosity)	1100
sintered stabilized zirconia (ca 5% porosity)	83
silica glass	107
vycor glass	69
pyrex glass	69
mullite porcelain	69
steatite porcelain	138
superduty fire-clay brick	5.2
magnesite brick	27.6
bonded silicon carbide (ca 20% porosity)	13.8
1090°C insulating firebrick (80-85% porosity)	0.28
1430°C insulating firebrick (ca 75% porosity)	1.17
1650°C insulating firebrick (ca 60% porosity)	2.0

It is also preferred to utilize a ceramic matrix composite material such as, for example, various ceramics that are reinforced with silicon carbide fibers or whiskers. Table 5, set forth below, lists properties of typical silicon carbide reinforced ceramics.

TABLE 5

SiC Reinforced Ceramics for Use in Mantle Layer(s)

Matrix	Reinforcement/vol %	Fracture toughness (ksi inches)½	Flexural strength (ksi)
Barium Osumilite	SiC whiskers/25	4 1	50-60
Corning 1723 Glass	SiC whiskers/25	1 9-3 1	30-50
Cordierite	SiC whiskers/20	3 4	40
$MoSi_2$	SiC whiskers/20	7 5	45
Mullite	SiC whiskers/20	4 2	65
Si_3N_4	SiC whiskers/10	5 9-8 6	60-75
Si_3N_4	SiC whiskers/30	6 8-9 1	50-65
Spinel	SiC whiskers/30	--	60
Toughened Al_2O_3	SiC whiskers/20	7 7-12 3	100-130

It is also preferred to provide a ceramic matrix of aluminum oxide, Al_2O_3, reinforced with silicon carbide fibers or whiskers. Typical properties of such a reinforced matrix are set forth below in Table 6.

TABLE 6

SiC Reinforced Al_2O_3 Ceramics for Use in Mantle Layer(s)

Reinforcement/vol %	Fracture strength (ksi)	Fracture toughness (ksi inches)½	Test temperature
SiC whiskers/10	65	6.5	RT
SiC whiskers/10	45	--	1830°F
SiC whiskers/20	95	6.8-8.2	RT
SiC whiskers/20	85	6.4-7.3	1830°F
SiC whiskers/40	120	5 5	RT
SiC whiskers/40	96	5.6	1830°F

Yet another preferred embodiment for the ceramic composite mantle is the use of a multidirectional continuous ceramic fiber dispersed within a ceramic composite. Typical properties of such substrates are set forth in Table 7 below.

TABLE 7

Multidirectional Continuous Ceramic Fibers in
Ceramic Composite for Use in Mantle Layer(s)

Material/properties

	$SiO_2/SiO_2$3-D	$Al_2O_3/Al_2O_3$3-D	$Al_2O_3/SiO_2$3-D	BN/Bn3-D
Reinforcement/(vol %)(10^3 psi)	SiO_2/50	Al_2O_3/30	Al_2O_3/30	BN/40
Tensile strength	3.87	10.3	10 8	3.6
Tensile modulus (10^6 psi)	2.26	5.26	4 90	2 23
Compressive strength (10^3 psi)	21.0	32.6	--	5.29
Compressive modulus (10^6 psi)	3.18	4.55	--	4.23
Thermal conductivity (BTU/hr/ft^2/°F/in)	4 6	11.2	4 7	62 4
Density (g/cm^3)	1.6	1 9	2 0	1.6

In forming the ceramic mantle, two approaches are primarily used. In a first preferred method, two ceramic half shells are formed. Each half shell utilizes a tongue and groove area along its bond interface region to improve bond strength. The shells are then adhesively bonded to one another by the use of one or more suitable adhesives known in the art.

In a second preferred method, a ceramic mantle layer is deposited over a core or hollow spherical substrate, both of which are described in greater detail below, by one of several deposition techniques. If a composite matrix utilizing fibers is to be formed, the fibers, if continuous, can be applied by winding the single or multi-strands onto the core or hollow spherical substrate, in either a wet or dry state. Using the wet method, the strand or strands pass through an epoxy resin bath prior to their winding around the core of the golf ball to a specific diameter. Either during or subsequent to winding, the wound core is compression molded using heat and moderate pressure in smooth spherical cavities. After de-molding, a dimpled cover is molded around the wound center using compression, injection, or transfer molding techniques. The ball is then trimmed, surface treated, stamped, and clear coated.

If the ceramic mantle layer is formed by a dry technique, the epoxy resin, such as in the dipping bath if the previously described wet method is used, can be impregnated into the fibers and molded as described above.

If the fiber is discontinuous, it can be applied to the core by simultaneously spraying a chopped fiber and a liquid epoxy resin to a revolving

core or spherical substrate. The wet, wound center is then cured by molding as previously described.

With regard to the use of discontinuous fibers, the critical factors are the length to diameter ratio of the fiber, the shear strength of the bond between the fiber and the matrix, and the amount of fiber. All of these variables effect the overall strength of the composite mantle.

The thickness of the ceramic mantle typically ranges from about 0.001 inch to about 0.070 inch. The preferred thickness ranges from about 0.005 inch to about 0.040 inch. The most preferred range is from about 0.010 inch to about 0.020 inch.

As the thickness of the ceramic layer increases, the weight and stiffness generally increases, and therefore, the PGA compression will also increase. This is typically the limiting factor, that is the PGA compression. Ball compressions over 110 PGA are generally undesirable. PGA compressions under 40 PGA are typically too soft. The overall ball compression can be adjusted by modifying or tailoring the core compression, i.e., a soft core requires a relatively thick mantle and a hard core requires a thin mantle but within the thicknesses described previously.

As noted, the mantle may comprise a ceramic composite material. In addition to dispersing glass and/or carbon fibers within various matrix materials, such as ceramics, epoxy, thermoset, and thermoplastics, other preferred fibers include boron carbide. It is also contemplated to utilize aramid (Kevlar), cotton, flax, jute, hemp, and silk fibers. The most preferred non-ceramic fibers are carbon, glass, and aramid fibers.

Typical properties for fibers suitable for forming reinforced materials are set forth below in Tables 8 and 9.

TABLE 8

Reinforced Composite Materials
for Use in Mantle Layer(s)

Fiber	Density (g/cm³)	Tensile strength GPa	ksi	Tensile modulus GPa	10⁶ psi
E-Glass	2.58	3.45	500	72.5	10 5
A-Glass	2.50	3.04	440	69.0	10.0
ECR-Glass	2.62	3.63	525	72.5	10 5
S-Glass	2.48	4.59	665	86.0	12.5

TABLE 9
Reinforced Composite Materials for Use in Mantle Layer(s)

Fiber	Precursor type	Density (g/cm³)	Tensile strength GPa	ksi	Tensile modulus GPa	10⁶ psi
AS-4	PAN	1.78	4.0	580	231	33.5
AS-6	PAN	1.82	4.5	652	245	35.5
IM-6	PAN	1.74	4.8	696	296	42.9
T300	PAN	1.75	3.31	480	228	32.1
T500	PAN	1.78	3.65	530	234	34.0
T700	PAN	1.80	4.48	650	248	36.0
T-40	PAN	1.74	4.50	652	296	42.9
Celion	PAN	1.77	3.55	515	234	34.0
Celion ST	PAN	1.78	4.34	630	234	34.0
XAS	PAN	1.84	3.45	500	234	34.0
HMS-4	PAN	1.78	3.10	450	338	49.0
PAN 50	PAN	1.81	2.41	355	393	57.0
HMS	PAN	1.91	1.52	220	341	49.4
G-50	PAN	1.78	2.48	360	359	52.0
GY-70	PAN	1.96	1.52	220	483	70.0
P-55	Pitch	2.0	1.73	250	379	55.0
P-75	Pitch	2.0	2.07	300	517	75.0
P-100	Pitch	2.15	2.24	325	724	100
HMG-50	Rayon	1.9	2.07	300	345	50.0
Thornel 75	Rayon	1.9	2.52	365	517	75.0

It is to be understood that one or more of these fibers could be

utilized in a ceramic, epoxy, thermoset, and/or thermoplastic matrix material in forming the mantle layer(s). Details of suitable epoxy, thermoset, and thermoplastic materials are set forth below.

The composite mantle may also be formed from various epoxy molding compounds including, for example, carbon or glass fibers dispersed within an epoxy matrix. Table 10, set forth below, lists typical properties of such epoxy molding compounds.

TABLE 10

Reinforced Epoxy Based Composite Materials for Use in Mantle Layer(s)

Material/Properties					
Matrix	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy
Reinforcement/(vol%)	Glass/60	Carbon/60	HS carbon/60	HM carbon/60	Shortglass/ 60
Density (g/cm³)	1.86-1.92	1.48-1.54	1.48-1.54	1.48-1.54	1.78-1.83
Tensile strength (10^3 psi)	35	30	32	18	11
Tensile modulus (10^6 psi)	--	--	--	--	--
Flexural strength (10^3 psi)	85	54	58	53	18
Flexural modulus (10^6 psi)	4.2	7.2	8.2	11.8	2.0
Compressive strength (10^3 psi)	42	36	44	31	28
Izod impact notched (ft lb/in.)	45	20	25	15	0.70
Coeff thermal expansion (10^{-6}/°F)	14	1.0	1.0	1.0	27
Conductivity (BTU/hr/ft²/°F/in.)	0.02	--	--	--	0.02
Heat deflection temp 264 psi (°F)	250	250	250	250	154
Flammability rating, UL	--	--	--	--	94V-1
Volume resistivity (ohm-cm)	7.5×10^{14}	--	--	--	9×10^{16}
Water absorption, 24 hr (%)	0.10	0.20	0.20	0.20	0.10

The composite mantle layer may also be formed from a composite material of glass fibers dispersed within a thermoset matrix wherein the

thermoset matrix is, for example, a polyimide material, silicone, vinyl ester, polyester, or melamine. Table 11, set forth below, lists typical properties of such composite thermoset molding materials.

TABLE 11

Reinforced Thermoset Composite Materials for Use in Mantle Layer(s)

Material/Properties

	Polyimide	Silicone	Vinyl ester	Polyester	Melamine
Matrix	Polyimide	Silicone	Vinyl ester	Polyester	Melamine
Reinforcement/(vol%)	Glass/60	Glass/60	Glass/60	Glass/60	Glass/60
Density (g/cm³)	1.95-2.00	2.00-2.05	1.84-1.90	1.84-1.90	1.79-1.84
Tensile strength (10³ psi)	21	4.0	39 0	8.0	8.0
Tensile modulus$_{eria}$ (10⁶ psi)	--	--	--	--	--
Flexural strength (10³ psi)	37	10	70	20	14
Flexural modulus (10⁶ psi)	3.1	2.0	2.8	2.2	2.2
Compressive strength (10³ psi)	32	11	42	20	42
Izod impact notched (ft lb/in.)	22	5.0	40	12	0.50
Coeff thermal expansion (10⁶/°F)	10	7.0	10	--	20
Conductivity (BTU/hr/ft²/°F/in.)	0.018	0.011	--	--	0.022
Heat deflection temp 264 psi (°F)	500	500	430	480	320
Flammability rating, UL	--	94V-0	--	--	94V-0
Volume resistivity (ohm-cm)	2.5 x 10¹⁶	--	--	--	--
Water absorption, 24 hr (%)	0.30	0.15	0.15	0.15	0.15

The preferred embodiment composite mantle layer may also be formed from various nylon molding compounds including, for example, glass or carbon fibers dispersed within a nylon matrix. Table 12 lists typical properties of such composite nylon mantles.

TABLE 12

Reinforced Nylon Composite Materials for use in Mantle Layer(s)

Material/Properties

Matrix	Nylon 6	Nylon 6	Nylon 6/6	Nylon 6/10	Nylon 6/10	Nylon 11
Reinforcement/(vol%)	Glass/20	Glass/40	Glass/40	Carbon/40	Glass/40	Glass/20
Density (g/cm^3)	1 27	1 46	1 46	1 33	1.40	1 18
Tensile strength (10^3 psi)	20	25	32	36	26.5	14
Tensile modulus (10^6 psi)	0 98	1 4	1.9	4 2	1 5	0 75
Flexural strength (10^3 psi)	23	31	40	52	38	17
Flexural modulus (10^6 psi)	0.70	1.3	1.7	3 4	1.3	0 53
Compressive strength (10^3 psi)	21	23	23	25	25	12.5
Izod impact notched (ft lb/in.)	1.3	2.5	2.6	1.6	3.3	1 4
Coeff thermal expansion (10^{-6}/°F)	23	13	19	8.0	11	40
Conductivity (BTU/hr/ft^2/°F/in.)	3.0	3 6	3.6	8.0	3.8	2 6
Heat deflection temp 264 psi (°F)	390	400	480	500	420	340
Flammability rating, UL	HB	HB	HB	HB	HB	HB
Volume resistivity (ohm-cm)	10^{14}	10^{14}	10^{14}	30	10^{12}	10^{13}
Water absorption, 24 hr (%)	1.3	1.0	0.7	0.4	0.23	0.19

The composite mantle layer may also be formed from a styrenic molding material, such as comprising glass or carbon fibers dispersed within a styrene material including, for example, an acrylonitrile-butadiene-styrene (ABS), polystyrene (PS), styrene-acrylonitrile (SAN), or styrene-maleic anhydride (SMA). Table 13, set forth below, lists typical properties for such materials.

TABLE 13

Reinforced Styrene-Based Composite Materials for Use in Mantle Layer(s)

Matl/Properties

Matrix	ABS	ABS	ABS	PS	SAN	SMA
Reinforcement/(vol%)	Glass/20	Glass/40	Carbon/40	Glass/40	Glass/40	Glass/40

Matl/Properties

Density (g/cm³)	1.18	1.38	1.24	1.38	1.40	1.40
Tensile strength (10³ psi)	13	18	17	14	20	14
Tensile modulus (10⁶ psi)	0.88	1 5	3.1	2 0	2 0	1 67
Flexural strength (10³ psi)	17	21	25	19	24	22.5
Flexural modulus (10⁶ psi)	0 80	1 3	2.8	1 6	1 8	1 37
Compressive strength (10³ psi)	13 5	19	19	17 5	22.0	--
Izod impact notched (ft lb/in.)	1.4	1.2	1.0	1.1	1.1	1.5
Coeff thermal expansion (10⁻⁶/°F)	20	13	12	17	15.5	--
Conductivity (BTU/hr/ft²/°F/in.)	1.4	1.6	3.8	2.2	2.1	--
Heat deflection temp 264 psi (°F)	220	240	240	210	217	250
Flammability rating, UL	HB	HB	HB	HB	HB	HB
Volume resistivity (ohm-cm)	10^{15}	10^{15}	30	10^{16}	10^{16}	--
Water absorption, 24 hr (%)	0.18	0.12	0.14	0.05	0 1	0.1

The preferred composite mantle may also be formed from a reinforced thermoplastic material, such as comprising glass fibers dispersed within acetal copolymer (AC), polycarbonate (PC), and/or liquid crystal polymer (LCP). Table 14, set forth below, lists typical properties for such materials.

TABLE 14

Reinforced Thermoplastic Composite Materials for Use in Mantle Layer(s)

Material/Properties

Matrix	AC	AC	PC	LCP
Reinforcement/(vol%)	Glass/20	Glass/40	Glass/40	Glass/30
Density (g/cm³)	1.55	1.74	1.52	1.57
Tensile strength (10³ psi)	12	13	21	16-29
Tensile modulus (10⁶ psi)	1.2	1.6	1.7	2.5-2.6

Material/Properties

Flexural strength (10^3 psi)	16.5	17.0	26.0	25-36
Flexural modulus (10^6 psi)	0 9	1.3	1 4	2 1-2.5
Compressive strength (10^3 psi)	12	11	22	--
Izod impact notched (ft lb/in.)	0.9	0.9	2.2	1.0-2.5
Coeff thermal expansion (10^{-6}/°F)	25	18	9.5	--
Conductivity (BTU/hr/ft^2/°F/in.)	2.0	2.3	2.4	--
Heat deflection temp 264 psi (°F)	325	328	300	445-600
Flammability rating, UL	HB	HB	V1	--
Volume resistivity (ohm-cm)	10^{14}	10^{14}	10^{16}	10^{16}
Water absorption, 24 hr (%)	0.5	1.0	0.07	--

The preferred embodiment composite material may also be formed from one or more thermoplastic molding compounds such as, for example, high density polyethylene (HDPE), polypropylene (PP), polybutylene terephthalate (PBT), or polyethylene terephthalate (PET) and including fibers of mica or glass. Table 15, set forth below, lists typical properties for such materials.

TABLE 15

Reinforced Thermoplastic Composite Materials for Use in Mantle Layer(s)

Material/Properties

Matrix	HDPE	HDPE	PP	PP	PBT	PET
Reinforcement/(vol%)	Glass/20	Glass/40	Glass/40	Mica/40	Glass/40	Glass/55
Density (g/cm^3)	1.10	1.28	1.23	1.26	1.63	1.80
Tensile strength (10^3 psi)	7.0	10	16	5.6	21.5	28.5
Tensile modulus (10^6 psi)	0.6	1.25	1.3	1.1	2.0	3.0
Flexural strength (10^3 psi)	9.0	12	19	9	30	43

Material/Properties

Flexural modulus (10^6 psi)	0.55	1.0	0.9	1 0	1.5	2.6
Compressive strength (10^3 psi)	5 0	7 5	13.0	7 0	20 0	28.5
Izod impact notched (ft lb/in.)	1 2	1 4	2.0	0 5	1 8	1 9
Coeff thermal expansion (10^{-6}/°F)	28	25	17.5	22	12	10
Conductivity (BTU/hr/ft^2/°F/in)	2.3	2.7	2.45	2.2	1.5	2.3
Heat deflection temp 264 psi (°F)	240	250	300	230	415	450
Flammability rating, UL	HB	HB	HB	HB	HB	HB
Volume resistivity (ohm-cm)	10^{16}	10^{16}	10^{15}	10^{16}	10^{16}	10^{16}
Water absorption, 24 hr (%)	0.01	0.022	0.06	0.03	0.08	0 04

The preferred embodiment composite mantle layer may also be formed from thermoplastic materials including various polyphenylenes such as polyphenylene ether (PPE), polyphenylene oxide (PPO), or polyphenylene sulfide (PPS) within which are dispersed fibers of glass or graphite. Typical properties of these materials are set forth below in Table 16.

TABLE 16

Reinforced Thermoplastic Composite Materials
for Use in Mantle Layer(s)

Material/Properties

Matrix	PPE-PPO	PPE-PPO	PPS	PPS	PPS
Reinforcement/(vol%)	Glass/20	Graphite/20	Glass/20	Glass/40	Graphite/40
Density (g/cm^3)	1.21	1.20	1.49	1 67	1.46
Tensile strength (10^3 psi)	13.5	15.0	14.5	20.0	26.0
Tensile modulus (10^6 psi)	1.0	1.0	1.3	2.0	4.8
Flexural strength (10^3 psi)	17.5	20.0	19.0	30.0	40 0
Flexural modulus (10^6 psi)	0.75	0.98	1.3	1.6	4.1
Compressive strength (10^3 psi)	--	17.0	22.5	25.0	27.0

Material/Properties

Izod impact notched (ft lb/in.)	2.0	1.6	1 4	1 4	1.2
Coeff thermal expansion (10^{-6}/°F)	20	12	16	12	8 0
Conductivity (BTU/hr/ft^2/°F/in.)	1 1	--	2 1	2 2	3.3
Heat deflection temp 264 psi (°F)	285	235	500	500	500
Flammability rating, UL	HB	--	VO	VO	VO
Volume resistivity (ohm-cm)	10^{17}	13.0	10^{16}	10^{16}	30
Water absorption, 24 hr (%)	0.06	--	0.02	0.02	0 02

Also preferred for the composite material are various polyaryl thermoplastic materials reinforced with glass fibers or carbon fibers. Table 17, set forth below, lists typical properties for such composite materials. It is to be noted that PAS is polyarylsulfone, PSF is Polysulfone, and PES is Polyethersulfone.

TABLE 17

Reinforced Polyaryl Thermoplastic Materials for Use in Mantle Layer(s)

Material/Properties

Matrix	PAS	PSF	PSF	PSF	PES	PES
Reinforcement/(vol%)	Glass/20	Glass/20	Glass/40	Carbon/40	Glass/40	Carbon/40
Density (g/cm^3)	1.51	1.38	1.56	1.42	1.68	1.52
Tensile strength (10^3 psi)	19	15	19	26	23	31
Tensile modulus (10^6 psi)	1.0	0.88	1.7	3.0	2.0	3.5
Flexural strength (10^3 psi)	27	20	25	35	31	42
Flexural modulus (10^6 psi)	0.9	0.7	1.2	2.4	1.6	3.2
Compressive strength (10^3 psi)	--	19	24	--	22	--
Izod impact notched (ft lb/in.)	1.1	1.1	1.6	1.3	1.5	1.4
Coeff thermal expansion (10^{-6}/°F)	--	17	13	--	14	--

Material/Properties

Conductivity (BTU/hr/ft²/°F/in.)	--	2.1	2.6	--	2.6	--
Heat deflection temp 264 psi (°F)	405	360	365	365	420	420
Flammability rating, UL	VO	V1	VO	V1	VO	VO
Volume resistivity (ohm-cm)	10^{16}	10^{15}	10^{15}	30	10^{16}	30
Water absorption, 24 hr (%)	0 4	0.24	0.25	0.25	0.30	0.30

Other thermoplastic materials may be used for the composite mantle including reinforced polyetherimide (PEI), or polyether etherketone (PEEK), reinforced with glass or carbon fibers. Table 18, set forth below, lists typical properties for such materials.

TABLE 18

Reinforced Thermoplastic Composite Materials for Use in Mantle Layer(s)

Material/Properties

Matrix	PEI	PEI	PEI	PEEK	PEEK
Reinforcement/(vol%)	Glass/20	Glass/40	Carbon/40	Glass/20	Carbon/40
Density (g/cm³)	1.41	1.59	1.44	1.46	1.46
Tensile strength (10^3 psi)	23	31	34	23	39
Tensile modulus (10^6 psi)	1.1	1.9	4.1	2.0	4.4
Flexural strength (10^3 psi)	32	43	48	36	54
Flexural modulus (10^6 psi)	0.95	1.6	3.2	1.1	3.2
Compressive strength (10^3 psi)	24	24.5	--	--	--
Izod impact notched (ft lb/in.)	1.6	2.1	1.2	1.5	1.7
Coeff thermal expansion (10^{-6}/°F)	15	11	--	14	--
Conductivity (BTU/hr/ft²/°F/in.)	1.7	1.8	--	--	--
Heat deflection temp 264 psi (°F)	410	410	410	550	550
Flammability rating, UL	VO	VO	VO	VO	VO

Material/Properties

Volume resistivity (ohm-cm)	10^{16}	10^{16}	10^{12}	10^{16}	30
Water absorption, 24 hr (%)	0.21	0.18	0 18	0 12	0 12

5   The thickness of a composite polymeric material based mantle generally ranges from about 0.001 inch to about 0.100 inch. The most preferred range is from about 0.010 inch to about 0.030 inch.

In forming the mantle from a polymeric material, two approaches are primarily used. In a first preferred method, two rigid polymeric half shells 10 are formed. Each half shell utilizes a tongue and groove area along its bond interface region to improve bond strength. The shells are then adhesively bonded to one another by the use of one or more suitable adhesives known in the art.

In a second preferred method, a polymeric mantle layer is 15 deposited over a core or hollow spherical substrate, both of which are described in greater detail herein, by one of several deposition techniques. If a composite matrix utilizing fibers is to be formed, the fibers, if continuous, can be applied by winding the single or multi-strands onto the core or hollow spherical substrate, in either a wet or dry state. Using the wet method, the strand or 20 strands pass through an epoxy or other suitable resin bath prior to their winding around the core of the golf ball to a specific diameter. Either during or subsequent to winding, the wound core is compression molded using heat and moderate pressure in smooth spherical cavities. After de-molding, a dimpled cover is molded around the wound center using compression, injection, or 25 transfer molding techniques. The ball is then trimmed, surface treated, stamped, and clear coated.

If the polymeric mantle layer is formed by a dry technique, the epoxy resin, such as in the dipping bath if the previously described wet method is used, can be impregnated into the fibers and molded as described above.

30   If the fiber is discontinuous, it can be applied to the core by simultaneously spraying a chopped fiber and a liquid resin to a revolving core or spherical substrate. The wet, wound center is then cured by molding as

previously described.

  With regard to the use of discontinuous fibers, the critical factors are the length to diameter ratio of the fiber, the shear strength of the bond between the fiber and the matrix, and the amount of fiber. All of these variables effect the overall strength of the composite mantle.

  In preparing the preferred embodiment golf balls, the polymeric outer cover layer, if utilized, may be molded (for instance, by injection molding or by compression molding) about the mantle.

Polymeric Hollow Sphere

  As noted, in another aspect, the present invention also provides a golf ball that optionally comprises a polymeric hollow sphere immediately adjacent to the mantle. The sphere may be disposed inward of the mantle, or be disposed outward of the mantle, relative to the center of the ball. The sphere may also be disposed immediately adjacent to the mantle, or have one or more layers of other materials separating it from the mantle. The polymeric hollow sphere can be formed from nearly any relatively strong plastic material. The thickness of the hollow sphere ranges from about 0.005 inches to about 0.010 inches. The hollow inner sphere can be formed using two half shells joined together via spin bonding, solvent welding, or other techniques known to those in the plastics processing arts. Alternatively, the hollow polymeric sphere may be formed via blow molding.

  A wide array of polymeric materials can be utilized to form the polymeric hollow sphere. Thermoplastic materials are generally preferred for use as materials for the shell. Typically, such materials should exhibit good flowability, moderate stiffness, high abrasion resistance, high tear strength, high resilience, and good mold release, among others.

  Synthetic polymeric materials which may be used in accordance with the present invention include homopolymeric and copolymer materials which may include: (1) Vinyl resins formed by the polymerization of vinyl chloride, or by the copolymerization of vinyl chloride with vinyl acetate, acrylic esters or vinylidene chloride; (2) Polyoldefins such as polyethylene, polypropylene, polybutylene, and copolymers such as polyethylene

methylacrylate, polyethylene ethylacrylate, polyethylene vinyl acetate, polyethylene methacrylic or polyethylene acrylic acid or polypropylene acrylic acid or terpolymers made from these and acrylate esters and their metal ionomers, polypropylene/EPDM grafted with acrylic acid or anhydride modified polyolefins; (3) Polyurethanes, such as are prepared from polyols and diisocyanates or polyisocyanates; (4) Polyamides such as poly(hexamethylene adipamide) and others prepared from diamines and dibasic acids, as well as those from amino acid such as poly(caprolactam), and blends of polyamides with SURLYN, polyethylene, ethylene copolymers, EDPA, etc; (5) Acrylic resins and blends of these resins with polyvinyl chloride, elastomers, etc.; (6) Thermoplastic rubbers such as the urethanes, olefinic thermoplastic rubbers such as blends of polyolefins with EPDM, block copolymers of styrene and butadiene, or isoprene or ethylene-butylene rubber, polyether block amides; (7) Polyphenylene oxide resins, or blends of polyphenylene oxide with high impact polystyrene; (8) Thermoplastic polyesters, such as PET, PBT, PETG, and elastomers sold under the trademark HYTREL by E.I DuPont De Nemours & Company of Wilmington, Del.; (9) Blends and alloys including polycarbonate with ABS, PBT, PET, SMA, PE elastomers, etc. and PVC with ABS or EVA or other elastomers; and (10) Blends of thermoplastic rubbers with polyethylene, polypropylene, polyacetal, nylon, polyesters, cellulose esters, etc.

It is also within the purview of this invention to add to the polymeric spherical substrate compositions of this invention materials which do not affect the basic novel characteristics of the composition. Among such materials are antioxidants, antistatic agents, and stabilizers.

Cover

The cover is preferably comprised of a hard, high-stiffness ionomer resin, most preferably a metal cation neutralized high acid ionomer resin containing more than 16% carboxylic acid by weight, or blend thereof. The cover has a Shore D hardness of about 65 or greater. The cover may be in the form of a single, unitary layer, or may utilize multiple cover layers.

With respect to the ionomeric cover composition of the invention, ionomeric resins are polymers containing interchain ionic bonding. As a result

of their toughness, durability, and flight characteristics, various ionomeric resins sold by E.I. DuPont de Nemours & Company under the trademark "Surlyn®" and more recently, by the Exxon Corporation (see U.S. Patent No. 4,911,451) under the trademark "Escor®" and the tradename "Iotek", have become the

5 materials of choice for the construction of golf ball covers over the traditional "balata" (trans-polyisoprene, natural or synthetic) rubbers.

Ionomeric resins are generally ionic copolymers of an olefin, such as ethylene, and a metal salt of an unsaturated carboxylic acid, such as acrylic acid, methacrylic acid or maleic acid. In some instances, an additional

10 softening comonomer such as an acrylate can also be included to form a terpolymer. The pendent ionic groups in the ionomeric resins interact to form ion-rich aggregates contained in a non-polar polymer matrix. The metal ions, such as sodium, zinc, magnesium, lithium, potassium, calcium, etc. are used to neutralize some portion of the acid groups in the copolymer resulting in a

15 thermoplastic elastomer exhibiting enhanced properties, i.e., improved durability, etc. for golf ball construction over balata.

The ionomeric resins utilized to produce cover compositions can be formulated according to known procedures such as those set forth in U. S. Patent No. 3,421,766 or British Patent No. 963,380, with neutralization effected

20 according to procedures disclosed in Canadian Patent Nos. 674,595 and 713,631, wherein the ionomer is produced by copolymerizing the olefin and carboxylic acid to produce a copolymer having the acid units randomly distributed along the polymer chain. Broadly, the ionic copolymer generally comprises one or more α-olefins and from about 9 to about 20 weight percent

25 of α, β-ethylenically unsaturated mono- or dicarboxylic acid, the basic copolymer neutralized with metal ions to the extent desired.

At least about 20% of the carboxylic acid groups of the copolymer are neutralized by the metal ions (such as sodium, potassium, zinc, calcium, magnesium, and the like) and exist in the ionic state. Suitable olefins for use

30 in preparing the ionomeric resins include ethylene, propylene, butene-1, hexene-1 and the like. Unsaturated carboxylic acids include acrylic, methacrylic, ethacrylic, α-chloroacrylic, crotonic, maleic, fumaric, itaconic acids, and the like. The ionomeric resins utilized in the golf ball industry are generally

copolymers of ethylene with acrylic (i.e., Escor®) and/or methacrylic (i.e., Surlyn®) acid. In addition, two or more types of ionomeric resins may be blended in to the cover compositions in order to produce the desired properties of the resulting golf balls.

5   The cover compositions which may be used in making the golf balls of the present invention are set forth in detail but not limited to those in copending U.S. Serial No. 07/776,803 filed October 15, 1991, and Serial No. 07/901,660 filed June 19, 1992, both incorporated herein by reference. In short, the cover material is comprised of hard, high stiffness ionomer resins, 10   preferably containing relatively high amounts of acid (i.e., greater than 16 weight percent acid, preferably from about 17 to about 25 weight percent acid, and more preferably from about 18.5 to about 21.5 weight percent) and at least partially neutralized with metal ions (such as sodium, zinc, potassium, calcium, magnesium and the like). The high acid resins are blended and melt processed 15   to produce compositions exhibiting enhanced hardness and coefficient of restitution values when compared to low acid ionomers, or blends of low acid ionomer resins containing 16 weight percent acid or less.

The preferred cover compositions are made from specific blends of two or more high acid ionomers with other cover additives which do not 20   exhibit the processing, playability, distance and/or durability limitations demonstrated by the prior art. However, as more particularly indicated below, the cover composition can also be comprised of one or more low acid ionomers so long as the molded covers exhibit a hardness of 65 or more on the Shore D scale.

25   The cover has a Shore D hardness of 65 or greater. Its composition includes a hard, high stiffness preferably high acid ionomer such as that sold by E.I. DuPont de Nemours & Company under the trademark "Surlyn®" and by Exxon Corporation under the trademark "Escor®" or tradename "Iotek", or blends thereof. In addition to the Surlyn® and Escor® or 30   Iotek ionomers, the cover may comprise any ionomer which either alone or in combination with other ionomers produces a molded cover having a Shore D hardness of at least 65. These include lithium ionomers or blends of ionomers with harder non-ionic polymers such as nylon, polyphenylene oxide and other

compatible thermoplastics. As briefly mentioned above, examples of cover compositions which may be used are set forth in detail in U.S. Patent No. 5,688,869 incorporated herein by reference. Of course, the cover compositions are not limited in any way to those compositions set forth in said copending applications. The high acid ionomers suitable for use in the present invention are ionic copolymers which are the metal, i.e., sodium, zinc, magnesium, etc., salts of the reaction product of an olefin having from about 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from about 3 to 8 carbon atoms. Preferably, the ionomeric resins are copolymers of ethylene and either acrylic or methacrylic acid. In some circumstances, an additional comonomer such as an acrylate ester (i.e., iso- or n-butylacrylate, etc.) can also be included to produce a softer terpolymer. The carboxylic acid groups of the copolymer are partially neutralized (i.e., approximately 10-75%, preferably 30-70%) by the metal ions. Each of the high acid ionomer resins included in the cover compositions of the invention contains greater than about 16% by weight of a carboxylic acid, preferably from about 17% to about 25% by weight of a carboxylic acid, more preferably from about 18.5% to about 21.5 % by weight of a carboxylic acid.

Although the cover composition preferably includes a high acid ionomeric resin and the scope of the patent embraces all known high acid ionomeric resins falling within the parameters set forth above, only a relatively limited number of these high acid ionomeric resins are currently available. In this regard, the high acid ionomeric resins available from E.I. DuPont de Nemours Company under the trademark "Surlyn®", and the high acid ionomer resins available from Exxon Corporation under the trademark "Escor®" or tradename "Iotek" are examples of available high acid ionomeric resins which may be utilized in the present invention.

The high acid ionomeric resins available from Exxon under the designation "Escor®" and or "Iotek", are somewhat similar to the high acid ionomeric resins available under the "Surlyn®" trademark. However, since the Escor®/Iotek ionomeric resins are sodium or zinc salts of poly(ethylene acrylic acid) and the "Surlyn®" resins are zinc, sodium, magnesium, etc. salts of poly(ethylene methacrylic acid), distinct differences in properties exist.

Examples of the high acid methacrylic acid based ionomers found suitable for use in accordance with this invention include Surlyn® AD-8422 (sodium cation), Surlyn® 8162 (zinc cation), Surlyn® SEP-503-1 (zinc cation), and Surlyn® SEP-503-2 (magnesium cation). According to DuPont, all of these

5 ionomers contain from about 18.5 to about 21.5% by weight methacrylic acid.

More particularly, Surlyn® AD-8422 is currently commercially available from DuPont in a number of different grades (i.e., AD-8422-2, AD-8422-3, AD-8422-5, etc.) based upon differences in melt index. According to DuPont, Surlyn® AD-8422 offers the following general properties when

10 compared to Surlyn® 8920 the stiffest, hardest of all on the low acid grades (referred to as "hard" ionomers in U.S. Patent No. 4,884,814):

TABLE 19

	LOW ACID	HIGH ACID	
	(15 wt% Acid)	(>20 wt% Acid)	
	SURLYN®	SURLYN®	SURLYN®
	8920	8422-2	8422-3
IONOMER			
Cation	Na	Na	Na
Melt Index	1.2	2.8	1.0
Sodium, Wt%	2.3	1.9	2.4
Base Resin MI	60	60	60
MP[1], °C	88	86	85
FP, °C	47	48.5	45
COMPRESSION MOLDING[2]			
Tensile Break, psi	4350	4190	5330
Yield, psi	2880	3670	3590
Elongation, %	315	263	289
Flex Mod, K psi	53.2	76.4	88.3
Shore D hardness	66	67	68

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[1]DSC second heat, 10°C/min heating rate.

[2]Samples compression molded at 150°C annealed 24 hours at 60°C. 8422-2, -3 were homogenized at 190°C before molding.

In comparing Surlyn® 8920 to Surlyn® 8422-2 and Surlyn® 8422-3, it is noted that the high acid Surlyn® 8422-2 and 8422-3 ionomers have a higher tensile yield, lower elongation, slightly higher Shore D hardness and much higher flexural modulus. Surlyn® 8920 contains 15 weight percent methacrylic acid and is 59% neutralized with sodium.

In addition, Surlyn® SEP-503-1 (zinc cation) and Surlyn® SEP-503-2 (magnesium cation) are high acid zinc and magnesium versions of the Surlyn® AD 8422 high acid ionomers. When compared to the Surlyn® AD 8422 high acid ionomers, the Surlyn SEP-503-1 and SEP-503-2 ionomers can be defined as follows:

TABLE 20

Surlyn® Ionomer	Ion	Melt Index	Neutralization %
AD 8422-3	Na	1.0	45
SEP 503-1	Zn	0.8	38
SEP 503-2	Mg	1.8	43

Furthermore, Surlyn® 8162 is a zinc cation ionomer resin containing approximately 20% by weight (i.e. 18.5-21.5% weight) methacrylic acid copolymer that has been 30-70% neutralized. Surlyn® 8162 is currently commercially available from DuPont.

Examples of the high acid acrylic acid based ionomers suitable for use in the present invention include the Escor® or Iotek high acid ethylene acrylic acid ionomers produced by Exxon. In this regard, Escor® or Iotek 959 is a sodium ion neutralized ethylene-acrylic acid copolymer. According to Exxon, Ioteks 959 and 960 contain from about 19.0 to about 21.0% by weight acrylic acid with approximately 30 to about 70 percent of the acid groups neutralized with sodium and zinc ions, respectively. The physical properties of these high acid acrylic acid based ionomers are as follows:

TABLE 21

PROPERTY	ESCOR® (IOTEK) 959	ESCOR® (IOTEK) 960
Melt Index, g/10 min	2.0	1.8
Cation	Sodium	Zinc
Melting Point, °F	172	174
Vicat Softening Point, °F	130	131
Tensile @ Break, psi	4600	3500
Elongation @ Break, %	325	430
Hardness, Shore D	66	57
Flexural Modulus, psi	66,000	27,000

Furthermore, as a result of the development by the inventors of a number of new high acid ionomers neutralized to various extents by several different types of metal cations, such as by manganese, lithium, potassium, calcium and nickel cations, several new high acid ionomers and/or high acid ionomer blends besides sodium, zinc and magnesium high acid ionomers or ionomer blends are now available for golf ball cover production. It has been found that these new cation neutralized high acid ionomer blends produce cover compositions exhibiting enhanced hardness and resilience due to synergies which occur during processing. Consequently, the metal cation neutralized high acid ionomer resins recently produced can be blended to produce substantially harder covered golf balls having higher C.O.R.'s than those produced by the low acid ionomer covers presently commercially available.

More particularly, several new metal cation neutralized high acid ionomer resins have been produced by the inventors by neutralizing, to various extents, high acid copolymers of an alpha-olefin and an alpha, beta-unsaturated carboxylic acid with a wide variety of different metal cation salts. This discovery is the subject matter of U.S. Application Serial No. 901,680, incorporated herein by reference. It has been found that numerous new metal cation neutralized high acid ionomer resins can be obtained by reacting a high acid copolymer (i.e. a copolymer containing greater than 16% by weight acid, preferably from about 17 to about 25 weight percent acid, and more preferably about 20 weight percent acid), with a metal cation salt capable of ionizing or neutralizing the

copolymer to the extent desired (i.e. from about 10% to 90%).

The base copolymer is made up of greater than 16% by weight of an alpha, beta-unsaturated carboxylic acid and an alpha-olefin. Optionally, a softening comonomer can be included in the copolymer. Generally, the

5   alpha-olefin has from 2 to 10 carbon atoms and is preferably ethylene, and the unsaturated carboxylic acid is a carboxylic acid having from about 3 to 8 carbons. Examples of such acids include acrylic acid, methacrylic acid, ethacrylic acid, chloroacrylic acid, crotonic acid, maleic acid, fumaric acid, and itaconic acid, with acrylic acid being preferred.

10   The softening comonomer that can be optionally included in the invention may be selected from the group consisting of vinyl esters of aliphatic carboxylic acids wherein the acids have 2 to 10 carbon atoms, vinyl ethers wherein the alkyl groups contains 1 to 10 carbon atoms, and alkyl acrylates or methacrylates wherein the alkyl group contains 1 to 10 carbon atoms. Suitable

15   softening comonomers include vinyl acetate, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, or the like.

Consequently, examples of a number of copolymers suitable for use to produce the high acid ionomers included in the present invention include,

20   but are not limited to, high acid embodiments of an ethylene/acrylic acid copolymer, an ethylene/methacrylic acid copolymer, an ethylene/itaconic acid copolymer, an ethylene/maleic acid copolymer, an ethylene/methacrylic acid/vinyl acetate copolymer, an ethylene/acrylic acid/vinyl alcohol copolymer, etc. The base copolymer broadly contains greater than 16% by weight

25   unsaturated carboxylic acid, from about 30 to about 83% by weight ethylene and from 0 to about 40% by weight of a softening comonomer. Preferably, the copolymer contains about 20% by weight unsaturated carboxylic acid and about 80% by weight ethylene. Most preferably, the copolymer contains about 20% acrylic acid with the remainder being ethylene.

30   Along these lines, examples of the preferred high acid base copolymers which fulfill the criteria set forth above, are a series of ethylene-acrylic copolymers which are commercially available from The Dow Chemical Company, Midland, Michigan, under the "Primacor" designation. These high

acid base copolymers exhibit the typical properties set forth below in Table 22.

TABLE 22

Typical Properties of Primacor

Ethylene-Acrylic Acid Copolymers

GRADE	PERCENT ACID	DENSITY, g/cc	MELT INDEX, g/10min	TENSILE YD. ST (psi)	FLEXURAL MODULUS (psi)	VICAT SOFT PT (°C)	SHORE D HARDNESS
ASTM		D-792	D-1238	D-638	D-790	D-1525	D-2240
5980	20.0	0.958	300.0	-	4800	43	50
5990	20.0	0.955	1300.0	650	2600	40	42
5990	20.0	0.955	1300.0	650	3200	40	42
5981	20.0	0.960	300.0	900	3200	46	48
5981	20.0	0.960	300.0	900	3200	46	48
5983	20.0	0.958	500.0	850	3100	44	45
5991	20.0	0.953	2600.0	635	2600	38	40

'The Melt Index values are obtained according to ASTM D-1238, at 190°C.

Due to the high molecular weight of the Primacor 5981 grade of the ethylene-acrylic acid copolymer, this copolymer is the more preferred grade utilized in the invention.

The metal cation salts utilized in the invention are those salts which provide the metal cations capable of neutralizing, to various extents, the carboxylic acid groups of the high acid copolymer. These include acetate, oxide or hydroxide salts of lithium, calcium, zinc, sodium, potassium, nickel, magnesium, and manganese.

Examples of such lithium ion sources are lithium hydroxide monohydrate, lithium hydroxide, lithium oxide and lithium acetate. Sources for the calcium ion include calcium hydroxide, calcium acetate and calcium oxide. Suitable zinc ion sources are zinc acetate dihydrate and zinc acetate, a blend of zinc oxide and acetic acid. Examples of sodium ion sources are sodium hydroxide and sodium acetate. Sources for the potassium ion include potassium hydroxide and potassium acetate. Suitable nickel ion sources are nickel acetate, nickel oxide and nickel hydroxide. Sources of magnesium include magnesium oxide, magnesium hydroxide, magnesium acetate. Sources of manganese include manganese acetate and manganese oxide.

The new metal cation neutralized high acid ionomer resins are produced by reacting the high acid base copolymer with various amounts of the metal cation salts above the crystalline melting point of the copolymer, such as at a temperature from about 200° F to about 500° F, preferably from about 250° F to about 350° F under high shear conditions at a pressure of from about 10 psi to 10,000 psi. Other well known blending techniques may also be used. The amount of metal cation salt utilized to produce the new metal cation neutralized high acid based ionomer resins is the quantity which provides a sufficient amount of the metal cations to neutralize the desired percentage of the carboxylic acid groups in the high acid copolymer. The extent of neutralization is generally from about 10% to about 90%.

As indicated below in Table 23, more specifically in Example 1 in U.S. Application Serial No. 901,680, a number of new types of metal cation neutralized high acid ionomers can be obtained from the above indicated process. These include new high acid ionomer resins neutralized to various extents with manganese, lithium, potassium, calcium and nickel cations. In addition, when a high acid ethylene/acrylic acid copolymer is utilized as the base copolymer component of the invention and this component is subsequently neutralized to various extents with the metal cation salts producing acrylic acid based high acid ionomer resins neutralized with cations such as sodium, potassium, lithium, zinc, magnesium, manganese, calcium and nickel, several new cation neutralized acrylic acid based high acid ionomer resins are produced.

TABLE 23

	Formulation No.	Wt-% Cation Salt	Wt-% Neutralization	Melt Index	C.O.R.	Shore D Hardness
	1(NaOH)	6.98	67.5	0.9	.804	71
	2(NaOH)	5.66	54.0	2.4	.808	73
5	3(NaOH)	3.84	35.9	12.2	.812	69
	4(NaOH)	2.91	27.0	17.5	.812	(brittle)
	5(MnAc)	19.6	71.7	7.5	.809	73
	6(MnAc)	23.1	88.3	3.5	.814	77
	7(MnAc)	15.3	53.0	7.5	.810	72
10	8(MnAc)	26.5	106	0.7	.813	(brittle)
	9(LiOH)	4.54	71.3	0.6	.810	74
	10(LiOH)	3.38	52.5	4.2	.818	72
	11(LiOH)	2.34	35.9	18.6	.815	72
	12(KOH)	5.30	36.0	19.3	Broke	70
15	13(KOH)	8.26	57.9	7.18	.804	70
	14(KOH)	10.7	77.0	4.3	.801	67
	15(ZnAc)	17.9	71.5	0.2	.806	71
	16(ZnAc)	13.9	53.0	0.9	.797	69
	17(ZnAc)	9.91	36.1	3.4	.793	67
20	18(MgAc)	17.4	70.7	2.8	.814	74
	19(MgAc)	20.6	87.1	1.5	.815	76
	20(MgAc)	13.8	53.8	4.1	.814	74
	21(CaAc)	13.2	69.2	1.1	.813	74
	22(CaAc)	7.12	34.9	10.1	.808	70

25 Controls: 50/50 Blend of Ioteks 8000/7030 C.O.R.=.810/65 Shore D Hardness
DuPont High Acid Surlyn® 8422 (Na) C.O.R.=.811/70 Shore D Hardness
DuPont High Acid Surlyn® 8162 (Zn) C.O.R.=.807/65 Shore D Hardness
Exxon High Acid Iotek EX-960 (Zn) C.O.R.=.796/65 Shore D Hardness

TABLE 23 (continued)

Formulatio n No.	Wt-% Cation Salt	Wt-% Neutralization	Melt Index	C.O.R.
23(MgO)	2.91	53.5	2.5	.813
24(MgO)	3.85	71.5	2.8	.808
25(MgO)	4.76	89.3	1.1	.809
26(MgO)	1.96	35.7	7.5	.815

Control for Formulations 23-26 is 50/50 Iotek 8000/7030,
C.O.R.=.814, Formulation 26 C.O.R. was normalized to that control accordingly

Formulation No.	Wt-% Cation Salt	Wt-% Neutralization	Melt Index	C.O.R.	Shore D Hardness
27(NiAc)	13.04	61.1	0.2	.802	71
28(NiAc)	10.71	48.9	0.5	.799	72
29(NiAc)	8.26	36.7	1.8	.796	69
30(NiAc)	5.66	24.4	7.5	.786	64

Control for Formulation Nos. 27-30 is 50/50 Iotek 8000/7030, C.O.R.=.807

When compared to low acid versions of similar cation neutralized ionomer resins, the new metal cation neutralized high acid ionomer resins exhibit enhanced hardness, modulus and resilience characteristics. These are properties that are particularly desirable in a number of thermoplastic fields, including the field of golf ball manufacturing.

When utilized in golf ball cover construction, it has been found that the new acrylic acid based high acid ionomers extend the range of hardness beyond that previously obtainable while maintaining the beneficial properties (i.e. durability, click, feel, etc.) of the softer low acid ionomer covered balls, such as balls produced utilizing the low acid ionomers disclosed in U.S. Patent Nos. 4,884,814 and 4,911,451, and the recently produced high acid blends disclosed in U.S. Patent No. 5,688,869. Moreover, as a result of the development of a number of new acrylic acid based high acid ionomer resins neutralized to various extents by several different types of metal cations, such as manganese, lithium, potassium, calcium and nickel cations, several new ionomers or

ionomer blends are now available for golf ball production. By using these high acid ionomer resins harder, stiffer golf balls having higher C.O.R.s, and thus longer distance, can be obtained.

As will be further noted in the Examples below, other ionomer resins may be used in the cover compositions, such as low acid ionomer resins, so long as the molded cover produces a Shore D hardness of 65 or more. Properties of some of these low acid ionomer resins are provided in the following Table 24:

TABLE 24

Typical Properties of Low Acid Escor® (Iotek) Ionomers

Resin Properties	ASTM Method	Units	4000	4010	8000	8020
Cation type			zinc	zinc	sodium	sodium
Melt index	D-1238	g/10 min.	2.5	1.5	0.8	1.6
Density	D-1505	kg/m³	963	963	954	960
Melting Point	D-3417	°C	90	90	90	87.5
Crystallization Point	D-3417	°C	62	64	56	53
Vicat Softening Point	D-1525	°C	62	63	61	64
% Weight Acrylic Acid			16	--	11	--
% of Acid Groups Cation Neutralized			30	--	40	--

Plaque Properties	ASTM Method	Units	4000	4010	8000	8020
(3 mm thick, compression molded)						
Tensile at Break	D-638	MPa	24	26	36	31.5
Yield point	D-638	MPa	none	none	21	21
Elongation at break	D-638	%	395	420	350	410
1% Secant modulus	D-638	MPa	160	160	300	350
Shore Hardness D	D-2240	--	55	55	61	58

Resin Properties	ASTM Method	Units	8030	7010	7020	7030
Cation type			sodium	zinc	zinc	zinc
Melt Index	D-1238	g/10 min.	2.8	0.8	1.5	2.5
Density	D-1505	kg/m^3	960	960	960	960
Melting Point	D-3417	oC	87.5	90	90	90
Crystallization Point	D-3417	oC	55	--	--	--
Vicat Softening Point	D-1525	oC	67	60	63	62.5
%Weight Acrylic Acid			--	--	--	--
% of Acid Groups Cation Neutralized			--	--	--	-

Plaque Properties (3 mm thick, compression molded)	ASTM Method	Units	8030	7010	7020	7030
Tensile at Break	D-638	MPa	28	38	38	38
Yield Point	D-638	MPa	23	none	none	
Elongation at Break	D-638	%	395	500	420	395
1% Secant modulus	D-638	MPa	390	--	--	--
Shore Hardness D	D-2240	--		59	57	55	55

In addition to the above noted ionomers, compatible additive materials may also be added to produce the cover compositions of the present invention. These additive materials include dyes (for example, Ultramarine Blue sold by Whitaker, Clark, and Daniels of South Painsfield, NJ), and pigments, i.e. white pigments such as titanium dioxide (for example Unitane 0-110) zinc oxide, and zinc sulfate, as well as fluorescent pigments. As indicated in U.S. Patent 4,884,814, the amount of pigment and/or dye used in conjunction with the polymeric cover composition depends on the particular base ionomer mixture utilized and the particular pigment and/or dye utilized. The concentration of the pigment in the polymeric cover composition can be from about 1% to about 10% as based on the weight of the base ionomer mixture. A more preferred range is from about 1% to about 5% as based on the weight of the base ionomer mixture. The most preferred range is from about 1% to about 3% as based on the weight of the base ionomer mixture. The most preferred pigment for use in accordance with this invention is titanium dioxide.

Moreover, since there are various hues of white, i.e. blue white, yellow white, etc., trace amounts of blue pigment may be added to the cover stock composition to impart a blue white appearance thereto. However, if

different hues of the color white are desired, different pigments can be added to the cover composition at the amounts necessary to produce the color desired.

In addition, it is within the purview of this invention to add to the cover compositions of this invention compatible materials which do not affect the basic novel characteristics of the composition of this invention. Among such materials are antioxidants (i.e. Santonox R), antistatic agents, stabilizers and processing aids. The cover compositions of the present invention may also contain softening agents, such as plasticizers, etc., and reinforcing materials such as glass fibers and inorganic fillers, as long as the desired properties produced by the golf ball covers of the invention are not impaired.

Furthermore, optical brighteners, such as those disclosed in U.S. Patent No. 4,679,795, may also be included in the cover composition of the invention. Examples of suitable optical brighteners which can be used in accordance with this invention are Uvitex OB as sold by the Ciba-Geigy Chemical Company, Ardsley, N.Y. Uvitex OB is thought to be 2,5-Bis(5-tert-butyl-2-benzoxazoly)thiophene. Examples of other optical brighteners suitable for use in accordance with this invention are as follows: Leucopure EGM as sold by Sandoz, East Hanover, N.J. 07936. Leucopure EGM is thought to be 7-(2n-naphthol(1,2-d)-triazol-2yl)-3phenyl-coumarin. Phorwhite K-20G2 is sold by Mobay Chemical Corporation, P.O. Box 385, Union Metro Park, Union, N.J. 07083, and is thought to be a pyrazoline derivative, Eastobrite OB-1 as sold by Eastman Chemical Products, Inc. Kingsport, Tenn., is thought to be 4,4-Bis(-benzoxaczoly)stilbene. The above-mentioned Uvitex and Eastobrite OB-1 are preferred optical brighteners for use in accordance with this invention.

Moreover, since many optical brighteners are colored, the percentage of optical brighteners utilized must not be excessive in order to prevent the optical brightener from functioning as a pigment or dye in its own right.

The percentage of optical brighteners which can be used in accordance with this invention is from about 0.01% to about 0.5% as based on the weight of the polymer used as a cover stock. A more preferred range is from about 0.05% to about 0.25% with the most preferred range from about

0.10% to about .020% depending on the optical properties of the particular optical brightener used and the polymeric environment in which it is a part.

Generally, the additives are admixed with a ionomer to be used in the cover composition to provide a masterbatch (M.B.) of desired concentration and an amount of the masterbatch sufficient to provide the desired amounts of additive is then admixed with the copolymer blends.

The above cover compositions, when processed according to the parameters set forth below and combined with soft cores at thicknesses defined herein to produce covers having a Shore D hardness of 65, provide golf balls with reduced spin rates. It is noted, however, that the high acid ionomer resins provide for more significant reduction in spin rate than that observed for the low acid ionomer resins.

The cover compositions and molded balls of the present invention may be produced according to conventional melt blending procedures. In this regard, the ionomeric resins are blended along with the masterbatch containing the desired additives in a Banbury type mixer, two-roll mill, or extruded prior to molding. The blended composition is then formed into slabs or pellets, etc. and maintained in such a state until molding is desired. Alternatively a simple dry blend of the pelletized or granulated resins and color masterbatch may be prepared and fed directly into the injection molding machine where homogenization occurs in the mixing section of the barrel prior to injection into the mold. If necessary, further additives such as an inorganic filler, etc., may be added and uniformly mixed before initiation of the molding process.

Moreover, golf balls of the present invention can be produced by molding processes currently well known in the golf ball art. Specifically, the golf balls can be produced by injection molding or compression molding the novel cover compositions about the soft polybutadiene cores to produce a golf ball having a diameter of about 1.680 inches or greater and weighing about 1.620 ounces. In an additional embodiment of the invention, larger molds are utilized to produce the thicker covered oversized golf balls. As indicated, the golf balls of the present invention can be produced by forming covers consisting of the compositions of the invention around the softer polybutadiene cores by conventional molding processes. For example, in compression molding, the

cover composition is formed via injection at about 380°F to about 450°F into smooth surfaced hemispherical shells which are then positioned around the core in a dimpled golf ball mold and subjected to compression molding at 200-300°F for 2-10 minutes, followed by cooling at 50-70°F for 2-10 minutes, to fuse the shells together to form an unitary ball. In addition, the golf balls may be produced by injection molding, wherein the cover composition is injected directly around the core placed in the center of a golf ball mold for a period of time at a mold temperature of from 50°F to about 100°F. After molding the golf balls produced may undergo various further finishing steps such as buffing, painting, and marking as disclosed in U.S. Patent No. 4,911,451.

The invention has been described with reference to the preferred embodiment. Obviously, modifications and alterations will occur to others upon a reading and understanding of the preceding detailed description. It is intended that the invention be construed as including all such alterations and modifications insofar as they come within the scope of the appended claims or the equivalents thereof.